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(71) Applicant: ECOPOL, L.L.C. [US/US]; 4545 McIntyre Street, Golden, CO 80403 (US).

(72) Inventors: VERSER, Dan, W.; 27451 Craig Lane, Golden, CO 80401 (US). SCHILLING, Kevin, H.; 13011 West 79th Place, Arvada, CO 80005 (US). CHEN, Xiaomao; 5427 Dover Street #C, Arvada, CO 80002 (US).

(74) Agents: TOMPKINS, Michael, L. et al.; Sheridan Ross P.C., Suite 3500, 1700 Lincoln Street, Denver, CO 80203 (US).

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(54) Title: METHOD FOR THE SYNTHESIS OF ENVIRONMENTALLY DEGRADABLE BLOCK COPOLYMERS

(57) Abstract

A method is provided for the synthesis of environmentally degradable block copolymers which includes the sequential polymerization of polymer-forming materials in the presence of one or more polymerization reaction accelerants and catalysts. The accelerants are a class of hydrogen-labile compounds which act as polymerization initiators and accelerate the polymerization rate significantly. The environmentally degradable block copolymers produced include those comprising segments of polymers of alkylene oxides, trimethylene carbonates, lactones and cyclic esters of hydroxycarboxylic acids.

METHOD FOR THE SYNTHESIS OF
ENVIRONMENTALLY DEGRADABLE BLOCK COPOLYMERS

5   FIELD OF THE INVENTION

The present invention relates to a method for synthesizing environmentally degradable block copolymers. In particular, the present invention includes a sequential method of at least two steps for polymerizing two or more

10   polymer-forming materials in the presence of a catalyst and polymerization accelerant for synthesizing environmentally degradable block copolymers.

BACKGROUND OF THE INVENTION

15   Block copolymers, i.e., polymers comprised of segments of two or more polymers linked to one another, can be synthesized from two or more base monomers in order to obtain a polymer having physical properties which ar different from those of the constituent polymers.   For

20   example, a hard, brittle polymer with a high tensile strength can be copolymerized with a soft, elastomeric polymer having low glass transition temperature (T_g) and low modulus in order to obtain a block copolymer having hard and soft segments which is both elastomeric and has a high

25   tensile strength.   Such block copolymers can be more suitable for uses, such as plastic bags and packaging films, than homopolymers synthesized from the constituent polymers.

U.S. Patent No. 5,342,395 by Jarrett et al., issued

30   August 30, 1994, and assigned to American Cyanamid Company discloses a method for producing block copolymers of

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lactide and ε-caprolactone, which consist of up to about 20 mole% ε-caprolactone.   Jarrett et al. disclose that ε-caprolactone can be polymerized in the presence of diethylene glycol and stannous octoate in a nitrogen purged

5   stirred reactor maintained at 200°C until maximum viscosity is achieved, after which time lactide is added to the reactor in order to produce the block copolymer. The entire process for producing the block copolymer purportedly takes between 3 and 4 hours, after which the products are ground

10   and dried under a vacuum for an additional 12 to 18 hours at 100°C and 0.2 mm Hg to remove the unreacted monomers.

There are, however, a number of disadvantages to known processes for producing block copolymers.   Most processes are commercially or economically unacceptable because of

15   the   length   of   time   it   takes   to   complete   the   block copolymerization reaction.   Also,   the   relatively   high polymerization temperatures used in known processes, i.e., temperatures up to and in excess of 200°C, can lead to color formation in the block copolymer produced due to the

20   prolonged reaction time.

Accordingly, it would be desirable to provide fast and efficient methods for producing environmentally degradable block copolymers which are commercially and economically acceptable.   It would be desirable to provide methods for

25   producing environmentally degradable block copolymers which do not result in excessive color formation in the block copolymers produced.

SUMMARY OF THE INVENTION

One aspect of the present invention is to provide fast and efficient methods for producing block copolymers, preferably environmentally degradable block copolymers,
5   which are commercially and economically acceptable and which do not result in excessive color formation in the environmentally degradable block copolymers produced.

It is a further aspect of the present invention to provide methods for synthesizing environmentally degradable
10   block copolymers which allow control over the properties of the block copolymers produced for specific end-uses.

It is yet a further aspect of the present invention to provide methods for synthesizing environmentally degradable block copolymers which give a high conversion of the
15   constituent monomers.

In accordance with the present invention, a method is provided for the synthesis of environmentally degradable block copolymers which includes the sequential addition of polymer-forming materials to a polymerization reactor and
20   the addition of one or more catalysts and one or more polymerization reaction accelerants as defined more fully below. Environmentally degradable block copolymers produced include those having soft and hard segments in both branched and star-shaped configurations.

25   Suitable polymer forming materials include, but are not limited to, alkylene oxides, trimethylene carbonates, lactones, and cyclic esters of hydroxycarboxylic acids such as lactide and glycolide.

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Suitable catalysts include, but are not limited to, tin, aluminum, yttrium and lanthanum based metal catalysts and mixtures thereof.

Suitable polymerization accelerants include, but are
5   not limited to, hydrogen-labile compounds such as alcohols, amino alcohols, diols, polyols, monoamino compounds, polyamino compounds and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

10   Figure 1 is a graphical representation of the tensile strength for various overall compositions of environmentally degradable block copolymers of ϵ-caprolactone and lactide synthesized according to the method of the present invention, using a pre-copolymer of
15   ϵ-caprolactone:lactide having a molar ratio of 80:20.

Figure 2 is a graphical representation of the tensile moduli for various overall compositions of environmentally degradable block copolymers of ϵ-caprolactone and lactide synthesized according to the method of the present
20   invention, using a pre-copolymer of ϵ-caprolactone:lactide having a molar ratio of 80:20.

Figure 3 is a graphical representation of the percent elongation for various overall compositions of environmentally degradable block copolymers of ϵ-
25   caprolactone and lactide synthesized according to the method of the present invention, using a pre-copolymer of ϵ-caprolactone:lactide having a molar ratio of 80:20.

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Figure 4 is a graphical representation of the tensile strength for various overall compositions of environmentally degradable block copolymers of ϵ-caprolactone and lactide synthesized according to the methods of the present invention without use of a pre-copolymer as the first polymer-forming material.

Figure 5 is a graphical representation of the tensile moduli for various overall compositions of environmentally degradable block copolymers of ϵ-caprolactone and lactide synthesized according to the methods of the present invention without use of a pre-copolymer as the first polymer-forming material.

Figure 6 is a graphical representation of the percent elongation for various overall compositions of environmentally degradable block copolymers of ϵ-caprolactone and lactide synthesized according to the methods of the present invention without use of a pre-copolymer as the first polymer-forming material.

Figure 7 is a graphical representation of the effect of the use of a polymerization accelerant in the second polymerization step according to the method of the present invention.

DETAILED DESCRIPTION

The present invention is directed to a method for synthesizing environmentally degradable block copolymers. The phrase "environmentally degradable," as used herein, refers to block copolymers capable of being at least about 98 percent, and preferably about 100 percent,

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hydrolytically degraded after discard. The environmentally degradable block copolymers are preferably at least about 98 percent hydrolytically degraded, and more preferably about 100 percent hydrolytically degraded, within about ten

5   years, more preferably within about five years, and even more preferably within about three years.   The environmentally degradable block copolymers can also be degraded by other mechanisms such as biological, chemical, mechanical, photo, and thermal degradation.

10   Preferably, the environmentally degradable block copolymers of the present invention can be distinguishable from biodegradable plastics which are used in the body (e.g., sutures, implants, and drug delivery devices), which are designed to undergo substantial, and often controlled,

15   degradation during use. In contrast, it is preferred that an environmentally degradable block copolymer of the present invention begins accelerated degradation after disposal, having exhibited only a minor amount of degradation during its operational lifetime.

20   The methods for synthesizing environmentally degradable block copolymers according to the present invention will now be described in more detail with respect to the synthesis of an environmentally degradable block copolymer comprised of two distinct polymer segments. It

25   is to be understood, however, that the methods of the present invention described below can be extended for the synthesis of environmentally degradable block copolymers containing three or more distinct polymer segments.

Although various polymerization techniques, such as solution polymerization and melt polymerization, can be used successfully to synthesize environmentally degradable block copolymers according to the present invention, it is

5   preferred that melt polymerization be used.   Melt polymerization is preferred because the material costs for melt polymerization are reduced relative to those for solution polymerization.   In particular, when using melt polymerization techniques the amount of by-products and

10   wastes produced are typically minimized.   Also, when using melt polymerization, less equipment is needed because there is no solvent to be removed from the synthesized block copolymers and treated or otherwise handled.   As a result, melt polymerization generates less volatile organics than

15   solution polymerization, making melt polymerization a technically less complicated and more environmentally sound process than solution polymerization.

The methods of the present invention for synthesizing environmentally degradable block copolymers include

20   providing a first polymer-forming material to a suitable polymerization reactor and polymerizing the first polymer-forming material in the presence of a catalyst and a polymerization accelerant to form a first polymer.   The method of the present invention further includes combining

25   a second polymer-forming material, a second catalyst and a second polymerization accelerant with the first polymer produced and polymerizing the second polymer-forming material.   Incorporation of a polymerization accelerant in

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the second polymerization step has been surprisingly found to substantially increase the polymerization rate of the second polymer-forming material, reducing the polymer melt residence time in the polymerization reactor, and

5   ultimately, substantially eliminates color formation in the block copolymers produced. Moreover, by varying the ratio of the catalyst to the polymerization accelerant that are added to the reaction, the reaction times for a desired conversion of monomers for a resultant block copolymer can

10   be reduced.

The environmentally degradable block copolymers produced include branched and star-shaped block copolymers which preferably include hard and soft polymer segments. The soft polymer segments are segments made of the first

15   polymer, and the hard segments are made of a polymer which contains repeating units of the second polymer-forming material. However, the hard segments can also include a portion of the first polymer-forming material incorporated with the second polymer-forming material. The

20   environmentally degradable block copolymer compositions formed typically also contain, unless removed, amounts of homopolymers of repeating units of the first and/or second polymer-forming materials. It is not always desirable or necessary to remove such homopolymers from the resulting

25   block copolymer. Surprisingly, it has been found that the block copolymers produced act as compatabilizers for the homopolymers, such that the resultant mixture is substantially uniform in appearance and properties.

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Suitable polymerization reactors include batch reactors such as continuously stirred tank reactors, continuous reactors such as single or twin-screw extruders, and combinations of batch and continuous reactors. Reactors

5   capable of high energy mixing, such as twin-screw extruders, are particularly useful as polymerization reactors in the present invention. Such extruders allow for continuous polymerization and more accurate temperature control over the polymerization than typical batch

10 polymerization reactors, particularly when the polymerization reaction is exothermic. Extruders are further preferred as polymerization reactors because they are capable of operation with very low to very high viscosity polymer melts.

15   Polymer-forming materials which are suitable for use in the present invention include those polymer-forming materials which form hard or soft polymer segments when polymerized. Preferred for use as a first polymer-forming material in the present invention are materials which form

20 soft or rubbery segments when polymerized, such as those materials having glass transition temperatures (T_g) less than about 10°C, and preferably less than about 0°C. Such first polymer-forming materials include, but are not limited to, alkylene oxides, trimethylene carbonates,

25 lactones, and mixtures thereof. More preferred first polymer-forming materials are trimethylene carbonate, ethylene glycol and lactones, including, but not limited to

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ϵ-caprolactone, δ-valerolactone, p-dioxanone and mixtures thereof.

Even more preferred as a first polymer-forming material are pre-copolymer materials, particularly when it is desired to control the physical and chemical properties of the environmentally degradable block copolymers synthesized. For example, a pre-copolymer material can comprise a first polymer-forming material and an additional polymer-forming material such that when polymerized, the first polymer is a copolymer having reduced crystallinity relative to a homopolymer of the first polymer-forming material. As a result, environmentally degradable block copolymers formed using the pre-copolymer as a first polymer forming material generally have different properties than those environmentally degradable block copolymers having the same overall molar ratio of polymer-forming materials, but were not synthesized using the pre-copolymer. Further, in some instances the block copolymers synthesized using pre-copolymer materials have characteristics which cannot be attained by synthesizing block copolymers from the same constituents without first forming the pre-copolymer material. Accordingly, the use of a pre-copolymer is very important in synthesizing block copolymers with desired characteristics.

The described ability to control the properties of the synthesized block copolymers using varying amounts of the constituent polymer-forming materials and pre-copolymer materials is illustrated in Figures 1-3. Figures 1-3 are

graphical representations of the tensile strength, tensile modulus, and percent elongation, respectively, for various overall compositions of environmentally degradable block copolymer of ε-caprolactone and lactide synthesized using

5   a pre-copolymer of ε-caprolactone:lactide having a molar ratio of 80:20. Figures 4-6 are graphical representations of the tensile strength, tensile modulus, and percent elongation, respectively, for various overall compositions of environmentally degradable block copolymer of ε-

10   caprolactone and lactide synthesized without using a pre-copolymer as the first polymer-forming material. As can be seen from a comparison of Figures 1 and 4, for the same overall molar ratios of ε-caprolactone:lactide, the two environmentally degradable block copolymers have very

15   different tensile strengths. At about a 40 mole% ε-caprolactone content, the block copolymer in Figure 1 has a tensile strength of about 3,000 psi compared to a tensile strength of about 5,000 psi for the block copolymer in Figure 4. As can be seen from a comparison of Figures 2

20   and 5, for the same overall molar ratios of ε-caprolactone:lactide, the two environmentally degradable block copolymers have very different moduli. At about a 40 mole% ε-caprolactone content, the block copolymer in Figure 2 has a tensile modulus of about 46 kpsi compared to a

25   tensile modulus of about 180 kpsi for the block copolymer in Figure 5. Similarly, as can be seen from a comparison of Figures 3 and 6, for the same overall molar ratios of ε-caprolactone:lactide, the two environmentally degradable

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block copolymers have very different percent elongation. At about a 32 mole% ε-caprolactone content, the block copolymer in Figure 3 has a percent elongation of about 130% compared to a percent elongation of about 380% for the

5   block copolymer in Figure 6.

Also illustrated by Figures 2 and 5, is that through the use of a pre-copolymer when synthesizing block copolymers, the constituent polymer materials can be used more efficiently to produce desired characteristics in the

10   resultant block copolymer. For example, at about 40 mole% ε-caprolactone content, the block copolymer synthesized using a pre-copolymer in Figure 2 has a tensile modulus within the range of from about 40 kpsi to about 50 kpsi. By comparison, the block copolymer in Figure 5, even at

15   about 50 mole% ε-caprolactone content, does not have a tensile modulus within the range of from about 40 kpsi to about 50 kpsi. Accordingly, when softness is a desired characteristic in the block copolymer, less ε-caprolactone needs to be used to achieve the desired characteristics

20   when a pre-copolymer is used to synthesize the block copolymer.

Preferred for use as pre-copolymer materials include, but are not limited to, mixtures of cyclic esters of hydroxycarboxylic acids with alkylene oxides, trimethylene

25   carbonates and lactones. More preferred for use as pre-copolymer materials include, but are not limited to, mixtures of cyclic esters of hydroxycarboxylic acids with trimethylene carbonate, ethylene glycol and lactones,

including, but not limited to, ε-caprolactone, δ-
valerolactone and p-dioxanone. Preferred cyclic esters of
hydroxycarboxylic acids include, but are not limited to,
lactide and glycolide. Examples of other suitable cyclic
5   esters include certain of the cyclic esters disclosed in
copending U.S. Patent Application Serial No. 08/127,907,
entitled "DEGRADABLE POLYDIOXANEONE-BASED MATERIALS". Even
more preferred for use as pre-copolymer materials include,
but are not limited to, mixtures of lactide with ε-
10   caprolactone.

When lactide and ε-caprolactone are used to form a
random copolymer as the first polymer, it is desirable to
combine lactide with the ε-caprolactone in amounts up to
about 40 mole%, and preferably in amounts in the range of
15   from about 20 mole% to about 25 mole%. Concentrations above
about 40 mole% lactide in the copolymer raises the glass
transition temperature of the copolymer above about 0°C,
making it less desirable as a first polymer when softness
of the resultant block copolymer is desired.

20   To enhance the polymerization rate of the first
polymer-forming material, a catalyst is added to the first
polymer-forming material in the polymerization reactor.
The term "catalyst," as used herein, refers to metal-
containing compounds which are capable of increasing the
25   polymerization rate of a polymer-forming material. Although
the term "catalyst" typically refers to materials which are
not consumed in a chemical reaction, the term "catalyst" is
used herein even though is not currently understood whether

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the described metal-containing compounds are consumed in
the polymerization reaction.

Typically, the catalyst which is used depends upon the
choice of the polymer-forming material with which it will
5   be combined.   For example, it is desirable to use a
catalyst which is compatible with the polymer-forming
material and does not substantially degrade the polymer-
forming material or the polymers formed from such materials
during processing.   Additionally, it is desirable to use a
10   catalyst which is non-toxic.   Suitable catalysts include,
but are not limited to, tin, aluminum, yttrium and
lanthanum based metal catalysts.   Preferred for use as
catalysts are stannous octoate $(Sn(Oct)_2)$, yttrium or
lanthanide series rare earth metal catalysts as are
15   described in U.S. Patent No. 5,028,667 by McLain et al.,
issued July 2, 1991, and mixtures thereof. More preferred
for use as a catalyst is stannous octoate.

The amount of the catalyst to be combined with the
first polymer-forming material can depend upon the amount
20   of the first polymer-forming material present, the toxicity
of the catalyst in a finished product and in the
environment after degradation of the product and to what
extent, if any, the catalyst can degrade the polymers
produced if too much catalyst is present during processing
25   of the polymers.   In most cases, the amount of catalyst
added to the first polymer-forming material is less than
about 1,000:1 moles first polymer-forming material:moles
catalyst, preferably less than about 2,000:1 moles first

polymer-forming material:moles catalyst, and more preferably less than about 2,500:1 moles first polymer-forming material:moles catalyst.

To further enhance the polymerization rate of the first polymer-forming material and initiate the formation of the environmentally degradable block copolymers, a polymerization accelerant is also combined with the first polymer-forming material and catalyst in the polymerization reactor. The phrase "polymerization accelerant," as used herein, refers to compounds which act as polymerization initiators (i.e., those compounds capable of providing chain propagating centers), thereby also accelerating the rate of polymerization, and are consumed in the polymerization reaction.

Typically, the polymerization accelerant which is used depends upon the choice of the polymer-forming material and catalyst with which it will be combined. For example, it is desirable to use a polymerization accelerant which is compatible with the polymer-forming material and catalyst and does not substantially degrade or assist in the degradation of the polymer-forming material or the polymers formed from such materials, such as during processing. Additionally, it is desirable to use a polymerization accelerant which is non-toxic. Further, the type of block copolymers produced, branched or star-shaped, is determined by the polymerization accelerant used. Accordingly, the choice of polymerization accelerant can also depend upon the type of block copolymer desired.

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Suitable polymerization accelerants include, but are not limited to, hydrogen-labile compounds such as alcohols, amino alcohols, diols, polyols, monoamino compounds, polyamino compounds and mixtures thereof.   Preferred
5   polymerization accelerants are polyols, including, but not limited to, glycerol, poly(ϵ-caprolactone) triol and mixtures thereof.   In general, star-shaped block copolymers are produced when polyols are used as the polymerization accelerant.

10   The type and amount of the polymerization accelerant to be combined with the first polymer-forming material can depend upon the desired final number average molecular weight (M_n) and weight average molecular weight (M_w) of the synthesized environmentally degradable block copolymers.
15   It has been found that the polymerization accelerant can affect the M_n and M_w of the resulting environmentally degradable block copolymers. While not fully understood, the effect of the polymerization accelerant on the M_n and M_w of the synthesized block copolymers appears to be dependent
20   upon the number of chain propagating centers on a single molecule of a polymerization accelerant.   While not intending to be bound by theory, it is believed that the greater the number of chain propagating centers on a single molecule of a polymerization accelerant, the higher the
25   final M_n and M_w of the resulting environmentally degradable block copolymers.   For example, when polyols are used as the polymerization accelerant and the propagating centers are the OH groups on the accelerant molecules, it is

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observed that for a given hydroxyl ([OH]) group concentration, the M_n and M_w of the resulting block copolymers are higher than for block copolymers synthesized using an alcohol as a polymerization accelerant.

5   In most cases, the amount of polymerization accelerant added to the first polymer-forming material is less than about 200:1 moles first polymer-forming material:moles polymerization accelerant, preferably less than about 300:1 moles first polymer-forming material:moles polymerization 10   accelerant, and more preferably less than about 500:1 moles first polymer-forming material:moles polymerization accelerant.

      Polymerization of the first polymer-forming material can be carried out at a suitable temperature and pressure 15   to obtain a first polymer material. It is desirable, however, that the temperature of the polymerization reaction be maintained within a temperature range which minimizes degradation of and color formation in the polymer being produced. Typically, such polymerization temperatures 20   are within the range of about 150°C to about 210°C. Preferred temperature ranges can depend upon the polymer-forming material being polymerized and the polymerization accelerant being used. In most cases, however, it is preferred that the polymerization temperature be maintained 25   within the range of about 160°C to about 200°C, and more preferably at a temperature within the range of about 170°C to about 190°C. If desired, the polymerization reaction can be carried out under inert atmospheric conditions, such

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as under a blanketing gas, to prevent moisture contamination which degrades the polymers being produced and to prevent contact of the polymerization mass with oxygen which can oxidize the polymers being produced. Such
5 blanketing gases include, but are not limited to argon and nitrogen.

The time required for substantial completion of the first polymerization reaction depends upon the polymerization rate for the first polymer-forming material,
10 which in turn depends upon the polymerization reaction parameters, including, but not limited to the catalyst used, the polymerization accelerant used and the polymerization temperatures and pressures. A convenient method of determining the extent of completion of the
15 polymerization reaction is by measuring the melt viscosity of the polymerization mass in the polymerization reactor. When maximum melt viscosity is achieved, the polymerization reaction is typically complete. Typically, the time it takes for a first polymer-forming material to reach maximum
20 melt viscosity is within the range of about 10 minutes to about 65 minutes, preferably the time it takes for a first polymer-forming material to reach maximum melt viscosity is within the range of about 10 minutes to about 40 minutes, and more preferably the time it takes for a first polymer-
25 forming material to reach maximum melt viscosity is within the range of about 10 minutes to about 30 minutes.

An important feature of the first polymerization step is that the chains of the first polymer formed during

polymerization are "living," i.e., they are reactive and able to continue to be polymerized. As a result, block copolymers can be formed by combining the first polymer with a second polymer-forming material. Accordingly, after

5   the first polymer material has been synthesized, a second polymer-forming material can be added to the first polymer in the same or an additional polymerization reactor. Though not necessary, it is desirable that the second polymer-forming material be capable of being polymerized at or near

10 about the same polymerization parameters (i.e., temperatures, pressures, etc.) as the first polymer-forming material. It is also desirable that the second polymer-forming material is not substantially degradable by the catalyst or polymerization accelerant utilized in

15 conjunction with the polymerization of the first polymer-forming material.

Polymer-forming materials which are suitable for use in the present invention as a second polymer-forming material include those polymer-forming materials which form

20 hard or soft polymer segments when polymerized. Preferred for use as second polymer-forming materials in the present invention are polymers which form hard segments when polymerized. Such second polymer-forming materials include, but are not limited to cyclic esters of hydroxycarboxylic

25 acids. More preferred materials for use in the present invention as second polymer-forming materials include lactide and glycolide. Even more preferred for use in the present invention as a second polymer-forming material is

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lactide. As used herein, the term "lactide" refers to the various isomeric forms of lactide, including, L-lactide, D-lactide, L,D-lactide and meso-lactide (M-lactide). When lactide is used as a second polymer-forming material, the

5   amounts of the various isomeric forms of lactide used can be varied to control the stereoregularity of the polylactide segments in the synthesized environmentally degradable block copolymers. Alternatively, the second polymer-forming material can also include up to about 5

10 mole% ϵ-caprolactone.

The amount of the second polymer-forming material added to the polymerization reactor depends upon the characteristics that are desired in the block copolymers to be produced. For example, to increase the elastomeric and

15 percent elongation qualities of the preferred environmentally degradable block copolymers of lactide and ϵ-caprolactone, it is desirable to increase the molar content of the ϵ-caprolactone to greater than about 5 mole% relative to lactide in the resulting block copolymer.

20 Preferably, however, the environmentally degradable block copolymers of lactide and ϵ-caprolactone contain in the range of from about 10 mole% to about 75 mole% ϵ-caprolactone. In general, to create a true block copolymer, enough of each polymer forming material must be added to

25 the polymerization reactor for the resulting block copolymers to contain greater than about 5 mole%, and preferably greater than about 10 mole%, of each polymer-forming material.

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Similar to the first polymerization reaction, a catalyst, as previously described is combined with the second polymer-forming material in order to enhance the rate of production of block copolymers. In a preferred

5   embodiment of the present invention, the catalyst combined with the second polymer-forming material is an additional amount of the same catalyst combined with the first polymer-forming material.

The amount of the catalyst to be combined with the

10 second polymer-forming material depends upon similar criteria used to determine the amount of catalyst combined with the first polymer-forming material, as previously described. In addition, consideration as to the type and concentration of catalyst already present in the first

15 polymer can effect the determination as to the amount of catalyst to be combined with the second polymer-forming material. In most cases, the amount of catalyst combined with the second polymer-forming material is less than about 1,000:1 moles second polymer-forming material:moles

20 catalyst, preferably less than about 2,000:1 moles second polymer-forming material:moles catalyst, and more preferably less than about 4,000:1 moles second polymer-forming material:moles catalyst.

A polymerization accelerant, as described previously,

25 is also combined with the second polymer-forming material in the polymerization reactor. In a preferred embodiment of the present invention, the polymerization accelerant combined with the second polymer-forming material and

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catalyst is an additional amount of the same polymerization accelerant combined with the first polymer-forming material.

The amount of the polymerization accelerant to be combined with the second polymer-forming material depends upon similar criteria used to determine the amount of polymerization accelerant combined with the first polymer-forming material, as previously described. However, additional consideration must be given as to the type and concentration of polymerization accelerant and catalyst already present in the first polymer, because these factors can effect the determination as to the amount of polymerization accelerant to be combined with the second polymer-forming material. In most cases, the amount of polymerization accelerant added to the polymerization reactor and combined with the second polymer-forming material is less than about 200:1 moles second polymer-forming material:moles polymerization accelerant, preferably less than about 300:1 moles second polymer-forming material:moles polymerization accelerant, and more preferably less than about 500:1 moles second polymer-forming material:moles polymerization accelerant.

After combining the second polymer-forming material and a polymerization accelerant in the polymerization reactor with the first polymer, polymerization can be carried out at a suitable temperature and pressure to obtain a block copolymer material. It is desirable, however, that the temperature and pressure of the

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polymerization reaction be maintained within temperature and pressure ranges which minimize degradation of and color formation in the block copolymer being produced. Typically, such polymerization temperatures are within the range of

5   about 150°C to about 210°C. Preferred temperature ranges can depend upon the polymer-forming material being polymerized and the polymerization accelerant being used. In most cases, however, it is preferred that the polymerization temperature be maintained within the range

10   of about 160°C to about 200°C, and more preferably at a temperature within the range of about 170°C to about 190°C. If desired, the polymerization reaction can be carried out under inert atmospheric conditions, such as under a blanketing gas, to prevent moisture contamination which

15   degrades the polymers being produced and to prevent contact of the polymerization mass with oxygen which can oxidize the polymers being produced.   Such blanketing gases include, but are not limited to argon and nitrogen.

The time required for the block copolymerization

20   reaction to go to substantial completion depends upon the polymerization rate for the second polymer-forming material, which in turn depends upon the polymerization reaction parameters, including, but not limited to the polymerization accelerants and catalysts used and the

25   polymerization temperatures. As stated previously, a convenient method of determining the extent of completion of the polymerization reaction is by measuring the melt viscosity of the polymerization mass in the polymerization

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reactor, and when maximum melt viscosity is achieved, the polymerization reaction is typically complete. Typically, the time it takes for the block copolymer mass to reach maximum melt viscosity is within the range of about 30 minutes to about 120 minutes, preferably is within the range of about 30 minutes to about 100 minutes, and more preferably is within the range of about 30 minutes to about 90 minutes. Accordingly, the total amount of time it takes to produce the environmentally degradable block copolymers is typically within the range of from about 40 minutes to about 170 minutes, preferably within the range of from about 40 minutes to about 130 minutes, and more preferably within the range of about 40 minutes to about 120 minutes.

The time with which it takes in order to produce block copolymers according to the present invention is an important aspect of the present invention. In contrast to known processes for producing block copolymers, the method described herein allows for the economical production of block copolymers due to the increased reaction rates, and without significant loss in weight average or number average molecular weight of the resulting block copolymer. The resulting reduced reaction times allow for the production of a final block copolymer that has substantially no color formation.

Typically, the conversion of the polymer-forming materials during polymerization of the block copolymers is in the range of from about 90% to about 98%, and preferably in the range of from about 92% to about 98%. As a result

of the high conversion of the polymer-forming materials, little of the polymer-forming materials are wasted. Further, less of the polymer-forming materials remain in the synthesized block copolymer which may need to be

5   removed.

In general, the environmentally degradable block copolymers synthesized have number average molecular weights (M_n) in the range of from about 60,000 to about 150,000 and weight average molecular weights (M_w) in the

10   range of from about 120,000 to about 300,000. In addition, such block copolymers typically exhibit at least two glass transition temperatures (T_g) which are representative of each of the polymers which comprise the block copolymer.

Following synthesis according to the methods of the

15   present invention, the environmentally degradable block copolymers can be treated in order to remove residual monomers and other impurities in the environmentally degradable block copolymers in order to render them suitable for their intended use. Such treatments include,

20   but are not limited to grinding of the block copolymer mass and subsequently drying the ground block copolymer mass to evolve undesired contaminants. In one embodiment of the present invention, the block copolymers synthesized can be dried for a time period within the range of from about 0.5

25   hours to about 20 hours at a temperature within the range of from about 100°C to about 180°C and a pressure within the range of from about 0.1 torr to about 5 torrs to remove residual monomers from the block copolymer mass. In another

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embodiment of the present invention, an extruder is used to continuously produce the environmentally degradable block copolymers and devolatilization of the monomers from the polymerization mass is accomplished using a

5   devolatilization zone in the reactor itself as is taught in the art, i.e., through the use of vents and reduced pressures in the extruder.

Importantly, the physical properties of the environmentally degradable block copolymers produced varies

10   widely and can be selectively controlled, as previously described. As a result, the environmentally degradable block copolymers synthesized according to the method of the present invention are suitable for use as a substitute for other, environmentally non-degradable polymers, including,

15   but not limited to, high density polyethylene, low density polyethylene, and polyvinyl chloride. For example, as shown in Figure 2, a degradable block copolymer of about 60 mole% lactide and about 40 mole% ϵ-caprolactone, synthesized using a pre-copolymer of lactide and ϵ-caprolactone has a

20   tensile modulus of about 40 kpsi to about 50 kpsi, which is within the range of the tensile moduli for high density polyethylene (about 60 kpsi) and low density polyethylene (about 30 kpsi).

In addition to the synthesis and purification of the

25   environmentally degradable block copolymers, the synthesized block copolymers can be further processed using conventional polymer processing techniques to obtain a product, such as, plastic bags, packaging films and solid

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cast, molded or extruded articles. It is preferred, however, that the environmentally degradable block copolymers synthesized according to the methods of the present invention can be injected, rolled, blown, cast or

5   pressed into films for use as plastic bags and packaging materials. As a result of the high melt strength which can be obtained with star-shaped environmentally degradable polymers synthesized according to the present invention, the block copolymers of the present invention are

10   particularly well-suited for use in blow molding applications.

Reference is now made to the following examples, which are intended to illustrate, and not to limit the present invention. Unless otherwise noted, all reaction times

15   given are for the polymerization to go to completion, which was estimated to be when the polymerization mass reached maximum melt viscosity. In addition, the residual monomer contents of the polymerization masses were determined by gas chromatography, and the M_n and M_w of the environmentally

20   degradable block copolymers were obtained by gel permeation chromatography.

EXAMPLES

COMPARATIVE EXAMPLE 1:

25   The following comparative example illustrates the production of an environmentally degradable block copolymer of ε-caprolactone and a lactide without use of a polymerization accelerant in the second polymerization step.

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ϵ-caprolactone, purchased from Aldrich Chemical Company was distilled in a vacuum over CaH_2 and stored in an argon gas environment. A 140 g sample of the ϵ-caprolactone thus prepared was charged to a Haake Rheomix 3000

5   polymerization reactor along with 0.275 g of stannous octoate, $Sn(Oct_2)$ obtained from Sigma Chemical Company, to give a molar ratio of ϵ-caprolactone:stannous octoate of about 1,472:1, and was reacted at 180°C and atmospheric pressure using a mixing rate of 36 rpm. During the

10 polymerization reaction, 9 g of polymer samples were taken from the reactor for analysis.

After 25 minutes, when the melt viscosity reached its maximum, L-lactide purchased from Purac Biochem, Gorinchem (Holland), which had been stored in an argon gas

15 environment after purchase, was added to the polymerization reactor in order to give a polymerization mass concentration of ϵ-caprolactone of about 35.7 mole% and a total polymer:catalyst molar ratio of 4,280:1, based on total ϵ-caprolactone and lactide. The reaction was

20 continued at the same temperature, pressure and mixing rate for an additional 110 minutes, until the melt viscosity reached its maximum. The resulting block copolymer had an ϵ-caprolactone concentration of 36.7 mole% (obtained through NMR analysis). The block copolymer produced was

25 pale yellow in color.

Table 1 below lists the results of the block copolymerization. The block copolymerization took a total of 135 minutes. The rate of lactide polymerization is shown graphically in Figure 7.

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TABLE 1

Reactor Feed	Time (Minutes)	Residual Monomer (wt%)		M_n	M_w
		ε-caprolactone	Lactide		
ε-Caprolactone & Sn(Oct)$_2$	10	23.37	-	86,065	151,925
	15	7.71	-	86,956	171,826
	20	4.64	-	78,641	166,939
	25	3.14	-	89,726	164,363
L-Lactide Added	55	0.90	40.44	111,959	174,944
	70	0.87	29.31	109,234	184,038
	95	0.67	13.71	122,390	201,975
	110	0.56	5.19	109,190	197,654

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EXAMPLE 2:

The following example illustrates the increased polymerization rate of the second polymer-forming material obtainable by the addition of catalyst and polymerization

5   accelerant in the second polymerization step according to the present invention.

A 124.2 g sample of ε-caprolactone prepared as described in the Example 1 was charged to a Haake Rheomix 3000 polymerization reactor along with stannous octoate to

10   give a molar ratio of ε-caprolactone:stannous octoate of about 3000:1. The ε-caprolactone was polymerized in the polymerization reactor at a temperature of 180°C and atmospheric pressure using a mixing rate of 36 rpm. During the polymerization, 14 g of polymer samples were taken from

15   the reactor for analysis.

After 32 minutes, L-lactide, was added to the polymerization reactor to give total concentration of ε-caprolactone in the polymerization mass of about 35.7 mole%. At the same time, stannous octoate and poly(ε-

20   caprolactone) triol were added to the polymerization reactor in a molar ratio of monomer:stannous octoate:[OH] concentration (based onpoly(ε-caprolactone) triol) of about 5,000:1:6. Polymerization was continued at the same temperature, pressure and mixing rate for an additional 53

25   minutes. The ε-caprolactone concentration in the resulting block copolymer was measured to be 36.5 mole% (by NMR analysis) and the total molar ratio of monomer:stannous octoate:[OH] concentration was 4,038/1/2.2, based on total

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ε-caprolactone and lactide. The block copolymer produced was colorless.

The results of the polymerization are shown below in Table 2. The overall block copolymerization took about 83

5 minutes. The rate of lactide polymerization is shown graphically in Figure 7. The rate of lactide polymerization in this Example 2 is greatly enhanced relative to the rate of lactide polymerization for Comparative Example 1 due to the addition of polymerization accelerant in the second

10 polymerization in Example 2.

TABLE 2

Reactor Feed	Time (Minutes)	Residual Monomer (wt%)		M_n	M_w
		ϵ-caprolactone	Lactide		
ϵ-Caprolactone & Sn(Oct)$_2$	30	13.97	-	61,945	126,074
L-Lactide & Sn(Oct)$_2$ & Poly(ϵ-caprolactone) triol Added	18	3.15	24.89	101,929	152,727
	28	2.91	13.92	90,143	158,325
	43	2.62	7.48	106,944	171,975
	53	2.27	5.01	89,289	162,821

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EXAMPLE 3:

The following example illustrates the increased polymerization rate of the second polymer-forming material obtainable by the addition of catalyst and polymerization
5   accelerant in the second polymerization step according to the present invention.

A 110 g sample of ϵ-caprolactone prepared as described in Example 1 was charged to a Haake Rheomix 3000 polymerization reactor along with stannous octoate to give
10   a molar ratio of ϵ-caprolactone:stannous octoate of about 3,000:1. The ϵ-caprolactone was polymerized in the polymerization reactor at a temperature of 180°C and atmospheric pressure using a mixing rate of 36 rpm. During the polymerization, 5 g of polymer samples were taken from
15   the reactor for analysis.

After 36 minutes, L-lactide, was added to the polymerization reactor to give total concentration of ϵ-caprolactone in the polymerization mass of about 35.7 mole%. At the same time, stannous octoate and glycerol
20   were added to the polymerization reactor in a molar ratio of monomer:stannous octoate:[OH] concentration (based on glycerol) of about 5,000/1/9. Polymerization was continued at the same temperature, pressure and mixing rate for an additional 54 minutes. The ϵ-caprolactone concentration in
25   the resulting block copolymer was measured to be 37.8 mole% (by NMR analysis) and the total molar ratio of monomer: stannous octoate:[OH] concentration was 4,032/1/3.2, based

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on total ϵ-caprolactone and lactide. The block copolymer produced was colorless.

The results of the polymerization are shown below in Table 3. The total block copolymerization took about 89
5   minutes. The rate of lactide polymerization is shown graphically in Figure 7. The rate of lactide polymerization in this Example 3 is greatly enhanced relative to the rate of lactide polymerization for Comparative Example 1 due to the addition of polymerization accelerant in the second
10   polymerization in Example 3.

TABLE 3

Reactor Feed	Time (Minutes)	Residual Monomer (wt%)		M_n	M_w
		ε-caprolactone	Lactide		
ε-Caprolactone & Sn(Oct)$_2$	35	13.69	-	74,038	131,473
L-Lactide & Sn(Oct)$_2$ & Glycerol Added	24	3.26	15.12	81,278	138,158
	49	3.12	3.12	99,654	154,905
	54	1.86	2.60	77,927	143,915

COMPARATIVE EXAMPLE 4:

The following comparative example illustrates the properties of an environmentally degradable block copolymer having an ϵ-caprolactone concentration of about 50 mole%.

5   A 150.4 g of ϵ-caprolactone prepared as described in Example 1 was charged to a Haake Rheomix 3000 polymerization reactor along with stannous octoate and glycerol to give a molar ratio of monomers:stannous octoate:[OH] concentration (based on glycerol) of about

10   3,000/1/7.5. The ϵ-caprolactone monomer was polymerized at 180°C and at atmospheric pressure using a mixing rate of 35 rpm. During this period of polymerization, about 6 g of samples were taken for analysis.

After 22 minutes, 179.5 g of L-lactide was added to

15   the polymerization reactor to give a total concentration of ϵ-caprolactone in the polymerization mass of about 50 mole%. Polymerization was continued at the same temperature, pressure and mixing rate for an additional 115 minutes. The ϵ-caprolactone concentration in the resulting

20   block copolymer was measured to be 51.1 mole% (by NMR analysis) and the total molar ratio of monomers:stannous octoate:[OH] concentration was 6,000/1/3.8. The results of polymerization are shown below in Table 4. The block copolymer produced was pale yellow in color.

25   The entire block copolymerization took about 180 minutes. The block copolymer exhibited a T_g at -52.4°C, corresponding to the glass transition of the poly(ϵ-caprolactone) soft phase. The polylactide hard phase of

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the block copolymer exhibited a melting temperature of
140.1°C with ΔH of 22.74 J/g, measured by differential
scanning calorimeter.   The melting peak of soft phase
overlapped the T_g of the hard phase; both were at about

5   50°C.   Tensile testing of the block copolymer yielded the
following: tensile modulus, 161 kpsi; stress at break,
5536 psi; elongation at break, 624%.

TABLE 4

Reactor Feed	Time (Minutes)	Residual Monomer (wt%)		M_n	M_w
		ε-caprolactone	Lactide		
ε-caprolactone, Sn(Oct)$_2$, glycerol	10	14.16		59,429	103,077
	16	2.54		57,962	118,270
	22	1.34		64,961	118,353
L-Lactide added	43	0.46	48.05	60,501	122,900
	68	0.45	33.36	73,253	132,430
	98	0.45	15.9	83,654	144,448
	138	0.45	11.33	90,151	167,125
	158	0.48	5.28	90,145	163,974

EXAMPLE 5:

The following example illustrates the synthesis of an environmentally degradable block copolymer with an overall feed ε-caprolactone concentration of about 50 mole%, and synthesized using an 80:20 molar ratio mixture of ε-caprolactone:L-lactide as the first polymer-forming material.

A mixture of 152.68 g of ε-caprolactone prepared as described in Example 1 and 48 g of L-lactide, resulting in a mixture of ε-caprolactone:L-lactide having the molar ratio 80:20, was charged to a Haake Rheomix 3000 polymerization reactor along with stannous octoate and glycerol to give a molar ratio of monomers:stannous octoate:[OH] concentration (based on glycerol) of about 4,240/1/6.6. The monomers were polymerized at 180°C and atmospheric pressure using a mixing rate of 36 rpm to form a random copolymer of ε-caprolactone and L-lactide. During this period of polymerization, about 10 g of sample was taken for analysis.

After 65 minutes, 136 g of L-lactide was added to the polymerization reactor to give a total concentration of ε-caprolactone in the polymerization mass of about 50 mole%. At the same time, stannous octoate and glycerol were added to the reactor in a molar ratio of monomers:stannous octoate:[OH] concentration of about 4,250/1/8.8. Polymerization was continued at the same temperature, pressure and mixing rate for an additional 35 minutes. The ε-caprolactone concentration in the resulting block

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copolymer was measured to be 49.4 mole% (by NMR analysis) and the total molar ratio of monomers:stannous octoate:[OH] concentration was 4,245/1/7.5. The results of polymerization are shown below in Table 5. The block copolymer

5   produced was colorless and nearly transparent, probably as a result of the reduced crystallinity of the soft phase.

The block copolymerization took about 100 minutes. The block copolymer showed two T_g's at -36.3 and 52.1°C, corresponding to the glass transitions of the ε-

10 caprolactone-rich soft phase and the L-lactide-rich hard phase, respectively. A melting temperature of 159.6°C with ΔH of 6.49 J/g, measured by differential scanning calorimeter corresponds to the melting point of the hard phase. The melting peak of the soft phase was not observed

15 because the crystallinity of the poly(ε-caprolactone) in the soft phase was substantially reduced by copolymerization with 20 mole% L-lactide. Tensile testing was conducted with the following results: Young's tensile modulus, 11.3 kpsi; stress at break, 1712 psi; elongation

20 at break, 620%.

Notably, the overall ε-caprolactone concentrations are nearly the same for the block copolymers synthesized in Examples 4 and 5. However, the block copolymer formed in Example 5 was much softer than that formed in Example 4,

25 with Young's tensile modulus of 11.3 kpsi and 161 kpsi, respectively. The differences in the moduli are probably also due to the elimination of crystallinity of the soft phase in Example 5.

TABLE 5

Reactor Feed	Time (Minutes)	Residual Monomer (wt%)		M_n	M_w
		ε-caprolactone	Lactide		
ε-caprolactone, L-lactide, Sn(Oct)$_2$, glycerol	35	40.8	3.21	42,491	76,976
	45	23.49	1.80	54,688	110,735
	55	8.75	0.69	71,331	137,217
	65	3.84	0.62	70,775	140,546
L-lactide, Sn(Oct)$_2$, glycerol	10	1.81	12.93	81,021	139,928
	25	1.87	5.72	85,763	151,564
	35	1.67	5.20	81,282	147,171

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The foregoing disclosure of the present invention has been presented for purposes of illustration and description. The description is not intended to limit the invention to the form disclosed herein. Consequently, the
5 invention and modifications commensurate with the above teachings and skill and knowledge of the relevant art are within the scope of the present invention. The preferred embodiment described above is also intended to explain the best mode known of practicing the invention and to enable
10 others skilled in the art to utilize the invention in various embodiments and with the various modifications required by their particular applications for use of the invention. It is intended that the appended claims be construed to include all alternative embodiments as
15 permitted by the prior art.

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What is claimed is:

1.   A   method   for   synthesizing   environmentally
degradable   block   copolymers,   the   method   comprising   the
steps of:

5   (a)   polymerizing a first polymer-forming material
selected   from   the   group   consisting   of   lactones,   cyclic
esters of hydroxycarboxylic acids, trimethylene carbonates,
alkylene oxides and mixtures thereof, in the presence of a
first   polymerization   accelerant   and   a   first   catalyst   to
10   form a first polymer;

           (b)   combining   said   first   polymer   with   a   second
polymer-forming material selected from the group consisting
of cyclic esters of hydroxycarboxylic acids and mixtures
thereof and a second polymerization accelerant and a second
15   catalyst; and

           (c)   polymerizing said second polymer-forming material
to form said environmentally degradable block copolymer.

           2.   The method as claimed in Claim 1, wherein said
environmentally   degradable   block   copolymer   has   soft
20   segments of said first polymer and hard segments of a
polymer comprising repeating units of said second polymer-
forming material.

           3.   The method as claimed in Claim 1, wherein said
steps of polymerizing comprise melt polymerization.

25   4.   The method as claimed in Claim 3, wherein said
step of melt polymerizing is accomplished using an
extruder.

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5.   The method as claimed in Claim 4, wherein said extruder comprises a twin screw extruder.

6.   The method as claimed in Claim 1, wherein said second polymerization accelerant and said second catalyst comprise an additional amount of said first polymerization accelerant and said first catalyst.

7.   The method as claimed in Claim 1, wherein said first and second polymerization accelerants are selected from the group consisting of alcohols, amino alcohols, diols, polyols, monoamino compounds, polyamino compounds and mixtures thereof.

8.   The method as claimed in Claim 1, wherein said first and said second catalysts comprise a metal catalyst selected from the group consisting of tin, aluminum, yttrium and lanthanum based metal catalysts.

9.   The method as claimed in Claim 1, wherein said first polymerization accelerant and said second polymerization accelerant are selected from the group consisting of glycerol and poly(ϵ-caprolactone) triol.

10.   The method as claimed in Claim 9, wherein said first catalyst and said second catalyst comprise stannous octoate.

11.   The method as claimed in Claim 1, wherein said first polymer-forming material comprises ϵ-caprolactone and said second polymer-forming material comprises lactide.

12.   The method as claimed in Claim 1, wherein said first polymer comprises a copolymer of a lactone and a cyclic ester of a hydroxycarboxylic acid.

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13.   The method as claimed in Claim 1, wherein said first polymer-forming material comprises a copolymer of ε-caprolactone and lactide.

14.   The method as claimed in Claim 13, wherein said second polymer-forming material comprises lactide.

15.   The method as claimed in Claim 14, wherein said second polymer-forming material comprises L-lactide and D-lactide.

16.   The method as claimed in Claim 1, wherein said second polymer-forming material comprises L-lactide and ε-caprolactone.

17.   The method as claimed in Claim 1, wherein said first polymer-forming material comprises ε-caprolactone and said second polymer-forming material comprises glycolide.

18.   The method as claimed in Claim 1, wherein said steps of polymerizing said first polymer-forming material and polymerizing said second polymer-forming material are carried out for a combined time of less than about 3 hours.

19.   The method as claimed in Claim 1, wherein said steps of polymerizing said first polymer-forming material and polymerizing said second polymer-forming material are carried out at temperatures within the range of from about 150°C to about 210°C.

20.   The method as claimed in Claim 1, wherein said environmentally degradable block copolymer comprises ε-caprolactone in the range of from about 5 mole% to about 50 mole%.

21.   The method as claimed in Claim 1, wherein said environmentally degradable block copolymer is selected from the group consisting of star-shaped and branched environmentally degradable block copolymers.

22.   The method as claimed in Claim 1, wherein said environmentally degradable block copolymer has a weight average molecular weight (M_w) in the range of from about 120,000 to about 300,000.

23.   The method as claimed in Claim 1, wherein said environmentally degradable block copolymer has a number average molecular weight (M_n) in the range of from about 60,000 to about 150,000.

24.   The method as claimed in Claim 1, comprising the further step of manufacturing a blown film from said environmentally degradable block copolymer.

25.   The method as claimed in Claim 1, wherein said environmentally degradable block copolymer is suitable for use as a substitute for other, non-degradable polymers selected from the group consisting of high density polyethylene, low density polyethylene and polyvinyl chloride.

26.   A method for synthesizing environmentally degradable block copolymers, the method comprising the steps of:

(a)   melt polymerizing ϵ-caprolactone in the presence of a polymerization accelerant and a catalyst at a temperature within the range of from about 150°C to about

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210°C for a time period of less than about 65 minutes to form a poly(ε-caprolactone) polymer;

(b)   mixing said poly(ε-caprolactone) polymer with an amount of a polymer-forming material selected from the
5   group consisting of lactide, glycolide and mixtures thereof and an additional amount of said polymerization accelerant and an additional amount of said catalyst, such that the resulting mixture comprises from about 50 mole% to about 95 mole% said polymer-forming material; and

10   (c)   melt polymerizing said polymer-forming material at a temperature within the range of from about 150°C to about 210°C for a time period of less than about two hours to form an environmentally degradable block copolymer.

27.   The method as claimed in Claim 26, wherein said
15   step of melt polymerizing is accomplished using a twin screw extruder.

28.   The method as claimed in Claim 26, wherein said polymerization accelerant is selected from the group consisting of alcohols, amino alcohols, diols, polyols,
20   monoamino compounds, polyamino compounds and mixtures thereof.

29.   The method as claimed in Claim 26, wherein said catalyst comprises a metal catalyst selected from the group consisting of tin, aluminum, yttrium and lanthanum based
25   metal catalysts.

30.   The method as claimed in Claim 26, wherein said environmentally degradable block copolymer has a weight

average molecular weight (M_v) in the range of from about 120,000 to about 300,000.

31.   The method as claimed in Claim 26, wherein said environmentally degradable block copolymer has a number average molecular weight (M_n) in the range of from about 60,000 to about 150,000.

32.   The method as claimed in Claim 26, comprising the further step of manufacturing a blown film from said environmentally degradable block copolymer.

33.   The method as claimed in Claim 26, wherein said environmentally degradable block copolymer is suitable for use as a substitute for other, non-degradable polymers selected from the group consisting of high density polyethylene, low density polyethylene and polyvinyl chloride.

34.   The method as claimed in Claim 26, wherein said steps of melt polymerizing are carried out for a combined time of less than about 3 hours.

35.   A   method   for   synthesizing environmentally degradable block copolymers, the method comprising the steps of:

(a)   providing a first environmentally degradable polymer-forming   material   having   a   glass   transition temperature of less than about 10°C to a polymerization reactor;

(b)   polymerizing said environmentally degradable first polymer-forming material in the presence of a first

catalyst and a first polymerization accelerant comprising a hydrogen-labile compound to form a first polymer;

(c) combining a second polymer-forming material comprising a cyclic ester of a hydroxycarboxylic acid with

5 said first polymer; and

(d) polymerizing said second polymer-forming material in the presence of a second polymerization catalyst and a second polymerization accelerant comprising a hydrogen-labile compound to form said environmentally degradable

10 block copolymer.

36. The method as claimed in Claim 35, wherein said first polymer-forming material comprises ϵ-caprolactone.

37. The method as claimed in Claim 35, wherein said cyclic ester of a hydroxycarboxylic acid comprises lactide.

15 38. The method as claimed in Claim 37, wherein said lactide comprises L-lactide and D-lactide.

39. The method as claimed in Claim 35, wherein said steps of polymerizing comprise melt polymerization.

40. The method as claimed in Claim 39, wherein said

20 step of melt polymerizing is accomplished using an extruder.

41. The method as claimed in Claim 35, wherein said second polymerization accelerant and said second catalyst comprise an additional amount of said first polymerization

25 accelerant and said first catalyst.

42. The method as claimed in Claim 35, wherein said first and second polymerization accelerants are selected from the group consisting of alcohols, amino alcohols,

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diols, polyols, monoamino compounds, polyamino compounds, and mixtures thereof.

43.   The method as claimed in Claim 35, wherein said first and second polymerization accelerants comprise polyols.

44.   The method as claimed in Claim 35, wherein said first and second catalysts comprise a metal catalyst selected from the group consisting of tin, aluminum, yttrium and lanthanum based metal catalysts.

45.   The method as claimed in Claim 35, wherein said environmentally degradable block copolymer comprises a block copolymer of ε-caprolactone and lactide.

46.   The method as claimed in Claim 35, wherein said environmentally degradable block copolymer comprises a star-shaped environmentally degradable block copolymer.

47.   The method as claimed in Claim 35, comprising the further step of manufacturing a blown film from said environmentally degradable block copolymer.

48.   The method as claimed in Claim 35, wherein said environmentally degradable block copolymer is suitable for use as a substitute for other, non-degradable polymers selected from the group consisting of high density polyethylene, low density polyethylene and polyvinyl chloride.
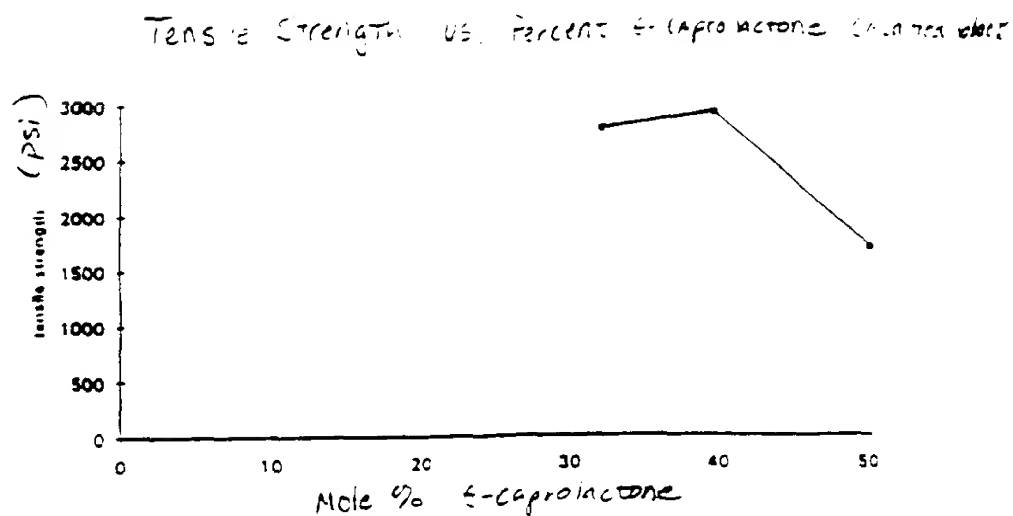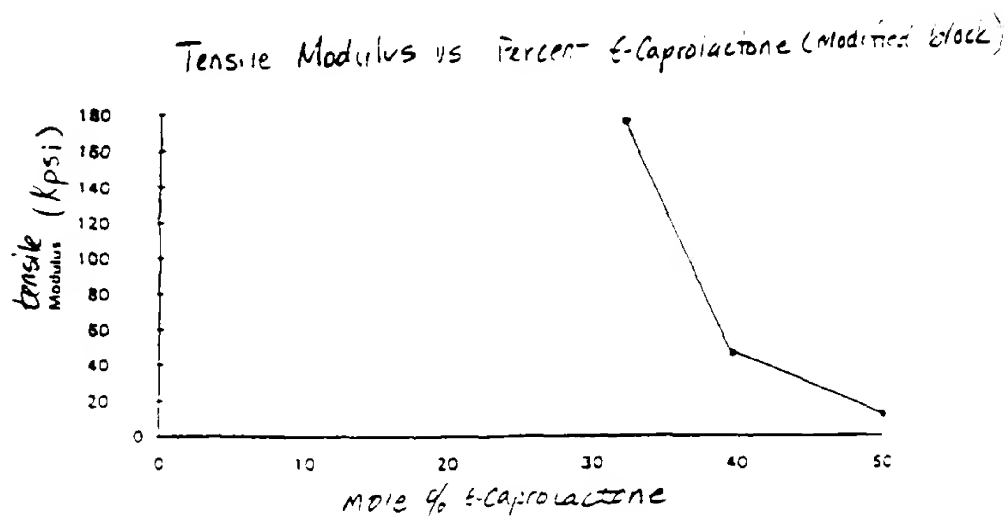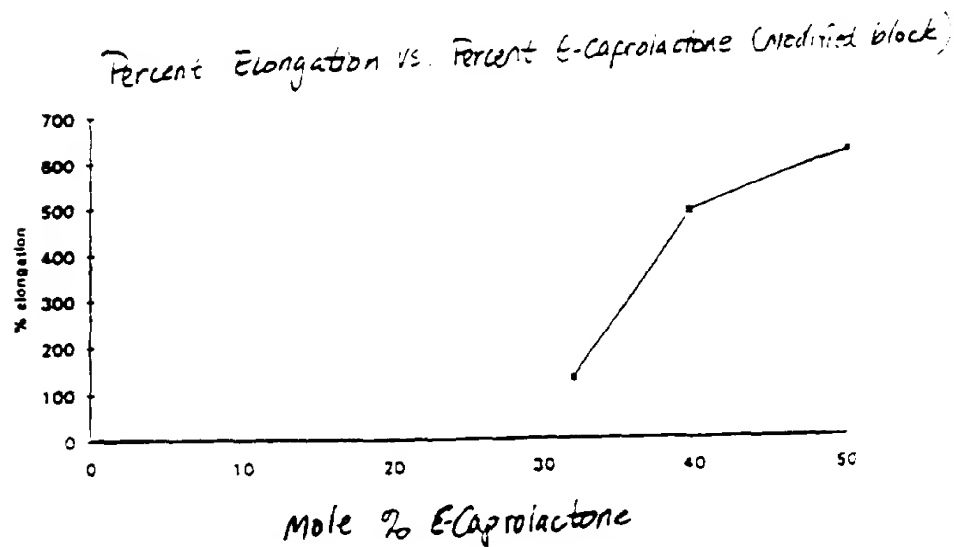
49.   An environmentally degradable block copolymer comprising from about 5 mole% to about 50 mole% hard segments of a polymer of ε-caprolactone and from about 50 mole% to about 95 mole% soft segments of a polymer having

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repeating units of a material selected from the group consisting of lactide and glycolide, wherein said block copolymer is substantially colorless.

50. A plastic bag comprising the environmentally degradable block copolymer claimed in Claim 49.

51. The environmentally degradable block copolymer claimed in Claim 49, wherein said block copolymer is suitable for use as a substitute for other, non-degradable polymers selected from the group consisting of high density polyethylene, low density polyethylene and polyvinyl chloride.

Tensile Strength vs. Percent ε-Caprolactone (modified block)

Fig. 1

Tensile Modulus vs Percent ε-Caprolactone (modified block)

Fig. 2

Percent Elongation vs. Percent ε-Caprolactone (modified block)

Fig. 3

Mole % ε-Caprolactone

Tensile Strength vs Percent ε- Caprolactone

Fig. 4

Tensile strength (psi) vs Mole % ε-caprolactone

Tensile Modulus vs. Percent ε-caprolactone

Fig. 5

tensile Modulus (kpsi) vs Mole % ε-caprolactone

Fig. 6

% Elongation vs Mole % ε-caprolactone

Figure 7

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION OF SUBJECT MATTER

IPC(6)   C08G 63/08, 63/02
US CL   :528/354, 355, 359, 361, 365, 370, 371
According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/354, 355, 359, 361, 365, 370, 371

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, 5,080,665 A (JARRETT et al.) 14 January 1992, see column 6, line 14 through column 7, line 22 and Examples 1-9.	1-51

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
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Date of the actual completion of the international search	Date of mailing of the international search report
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Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	MELVYN I. MARQUIS
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2351

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(72) Inventors: VERSER, Dan, W.; 27451 Craig Lane, Golden, CO 80401 (US). SCHILLING, Kevin, H., 13011 West 79th Place, Arvada, CO 80005 (US). CHEN, Xiaomao; 5427 Dover Street #C, Arvada, CO 80002 (US).

(74) Agents: TOMPKINS, Michael, L. et al.; Sheridan Ross P.C., Suite 3500, 1700 Lincoln Street, Denver, CO 80203 (US).

(54) Title: METHOD FOR THE SYNTHESIS OF ENVIRONMENTALLY DEGRADABLE BLOCK COPOLYMERS

(57) Abstract

A method is provided for the synthesis of environmentally degradable block copolymers which includes the sequential polymerization of polymer-forming materials in the presence of one or more polymerization reaction accelerants and catalysts. The accelerants are a class of hydrogen-labile compounds which act as polymerization initiators and accelerate the polymerization rate significantly. The environmentally degradable block copolymers produced include those comprising segments of polymers of alkylene oxides, trimethylene carbonates, lactones and cyclic esters of hydroxycarboxylic acids.

METHOD FOR THE SYNTHESIS OF
ENVIRONMENTALLY DEGRADABLE BLOCK COPOLYMERS

5   FIELD OF THE INVENTION

The present invention relates to a method for synthesizing environmentally degradable block copolymers. In particular, the present invention includes a sequential method of at least two steps for polymerizing two or more

10   polymer-forming materials in the presence of a catalyst and polymerization accelerant for synthesizing environmentally degradable block copolymers.

BACKGROUND OF THE INVENTION

15   Block copolymers, i.e., polymers comprised of segments of two or more polymers linked to one another, can be synthesized from two or more base monomers in order to obtain a polymer having physical properties which are different from those of the constituent polymers.   For

20   example, a hard, brittle polymer with a high tensile strength can be copolymerized with a soft, elastomeric polymer having low glass transition temperature (T_g) and low modulus in order to obtain a block copolymer having hard and soft segments which is both elastomeric and has a high

25   tensile strength.   Such block copolymers can be more suitable for uses, such as plastic bags and packaging films, than homopolymers synthesized from the constituent polymers.

U.S. Patent No. 5,342,395 by Jarrett et al., issued

30   August 30, 1994, and assigned to American Cyanamid Company discloses a method for producing block copolymers of

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lactide and ε-caprolactone, which consist of up to about 20 mole% ε-caprolactone.   Jarrett et al. disclose that ε-caprolactone can be polymerized in the presence of diethylene glycol and stannous octoate in a nitrogen purged

5   stirred reactor maintained at 200°C until maximum viscosity is achieved, after which time lactide is added to the reactor in order to produce the block copolymer. The entire process for producing the block copolymer purportedly takes between 3 and 4 hours, after which the products are ground

10   and dried under a vacuum for an additional 12 to 18 hours at 100°C and 0.2 mm Hg to remove the unreacted monomers.

There are, however, a number of disadvantages to known processes for producing block copolymers.   Most processes are commercially or economically unacceptable because of

15   the length of time it takes to complete the block copolymerization reaction.   Also, the relatively high polymerization temperatures used in known processes, i.e., temperatures up to and in excess of 200°C, can lead to color formation in the block copolymer produced due to the

20   prolonged reaction time.

Accordingly, it would be desirable to provide fast and efficient methods for producing environmentally degradable block copolymers which are commercially and economically acceptable.   It would be desirable to provide methods for

25   producing environmentally degradable block copolymers which do not result in excessive color formation in the block copolymers produced.

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SUMMARY OF THE INVENTION

One aspect of the present invention is to provide fast and efficient methods for producing block copolymers, preferably environmentally degradable block copolymers, which are commercially and economically acceptable and which do not result in excessive color formation in the environmentally degradable block copolymers produced.

It is a further aspect of the present invention to provide methods for synthesizing environmentally degradable block copolymers which allow control over the properties of the block copolymers produced for specific end-uses.

It is yet a further aspect of the present invention to provide methods for synthesizing environmentally degradable block copolymers which give a high conversion of the constituent monomers.

In accordance with the present invention, a method is provided for the synthesis of environmentally degradable block copolymers which includes the sequential addition of polymer-forming materials to a polymerization reactor and the addition of one or more catalysts and one or more polymerization reaction accelerants as defined more fully below. Environmentally degradable block copolymers produced include those having soft and hard segments in both branched and star-shaped configurations.

Suitable polymer forming materials include, but are not limited to, alkylene oxides, trimethylene carbonates, lactones, and cyclic esters of hydroxycarboxylic acids such as lactide and glycolide.

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Suitable catalysts include, but are not limited to, tin, aluminum, yttrium and lanthanum based metal catalysts and mixtures thereof.

Suitable polymerization accelerants include, but are not limited to, hydrogen-labile compounds such as alcohols, amino alcohols, diols, polyols, monoamino compounds, polyamino compounds and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graphical representation of the tensile strength for various overall compositions of environmentally degradable block copolymers of ϵ-caprolactone and lactide synthesized according to the method of the present invention, using a pre-copolymer of ϵ-caprolactone:lactide having a molar ratio of 80:20.

Figure 2 is a graphical representation of the tensile moduli for various overall compositions of environmentally degradable block copolymers of ϵ-caprolactone and lactide synthesized according to the method of the present invention, using a pre-copolymer of ϵ-caprolactone:lactide having a molar ratio of 80:20.

Figure 3 is a graphical representation of the percent elongation for various overall compositions of environmentally degradable block copolymers of ϵ-caprolactone and lactide synthesized according to the method of the present invention, using a pre-copolymer of ϵ-caprolactone:lactide having a molar ratio of 80:20.

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Figure 4 is a graphical representation of the tensile
strength   for   various   overall   compositions   of
environmentally degradable block copolymers of ϵ-
caprolactone and lactide synthesized according to the
5   methods of the present invention without use of a pre-
copolymer as the first polymer-forming material.

Figure 5 is a graphical representation of the tensile
moduli for various overall compositions of environmentally
degradable block copolymers of ϵ-caprolactone and lactide
10   synthesized according to the methods of the present
invention without use   of a pre-copolymer as the first
polymer-forming material.

Figure 6 is a graphical representation of the percent
elongation   for   various   overall   compositions   of
15   environmentally degradable block copolymers of ϵ-
caprolactone and lactide synthesized according to the
methods of the present invention without use   of a pre-
copolymer as the first polymer-forming material.

Figure 7 is a graphical representation of the effect
20   of the use of a polymerization accelerant in the second
polymerization step according to the method of the present
invention.

DETAILED DESCRIPTION

The present invention is directed to a method for
25   synthesizing environmentally degradable block copolymers.
The phrase "environmentally degradable," as used herein,
refers to block copolymers capable of being at least about
98   percent,   and   preferably   about   100   percent,

hydrolytically degraded after discard. The environmentally degradable block copolymers are preferably at least about 98 percent hydrolytically degraded, and more preferably about 100 percent hydrolytically degraded, within about ten

5   years, more preferably within about five years, and even more preferably within about three years. The environmentally degradable block copolymers can also be degraded by other mechanisms such as biological, chemical, mechanical, photo, and thermal degradation.

10   Preferably, the environmentally degradable block copolymers of the present invention can be distinguishable from biodegradable plastics which are used in the body (e.g., sutures, implants, and drug delivery devices), which are designed to undergo substantial, and often controlled,

15   degradation during use. In contrast, it is preferred that an environmentally degradable block copolymer of the present invention begins accelerated degradation after disposal, having exhibited only a minor amount of degradation during its operational lifetime.

20   The methods for synthesizing environmentally degradable block copolymers according to the present invention will now be described in more detail with respect to the synthesis of an environmentally degradable block copolymer comprised of two distinct polymer segments. It

25   is to be understood, however, that the methods of the present invention described below can be extended for the synthesis of environmentally degradable block copolymers containing three or more distinct polymer segments.

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Although various polymerization techniques, such as solution polymerization and melt polymerization, can be used successfully to synthesize environmentally degradable block copolymers according to the present invention, it is
5   preferred that melt polymerization be used. Melt polymerization is preferred because the material costs for melt polymerization are reduced relative to those for solution polymerization. In particular, when using melt polymerization techniques the amount of by-products and
10   wastes produced are typically minimized. Also, when using melt polymerization, less equipment is needed because there is no solvent to be removed from the synthesized block copolymers and treated or otherwise handled. As a result, melt polymerization generates less volatile organics than
15   solution polymerization, making melt polymerization a technically less complicated and more environmentally sound process than solution polymerization.

The methods of the present invention for synthesizing environmentally degradable block copolymers include
20   providing a first polymer-forming material to a suitable polymerization reactor and polymerizing the first polymer-forming material in the presence of a catalyst and a polymerization accelerant to form a first polymer. The method of the present invention further includes combining
25   a second polymer-forming material, a second catalyst and a second polymerization accelerant with the first polymer produced and polymerizing the second polymer-forming material. Incorporation of a polymerization accelerant in

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the second polymerization step has been surprisingly found
to substantially increase the polymerization rate of the
second polymer-forming material, reducing the polymer melt
residence time in the polymerization reactor, and
5 ultimately, substantially eliminates color formation in the
block copolymers produced. Moreover, by varying the ratio
of the catalyst to the polymerization accelerant that are
added to the reaction, the reaction times for a desired
conversion of monomers for a resultant block copolymer can
10 be reduced.

The environmentally degradable block copolymers
produced include branched and star-shaped block copolymers
which preferably include hard and soft polymer segments.
The soft polymer segments are segments made of the first
15 polymer, and the hard segments are made of a polymer which
contains repeating units of the second polymer-forming
material. However, the hard segments can also include a
portion of the first polymer-forming material incorporated
with the second polymer-forming material. The
20 environmentally degradable block copolymer compositions
formed typically also contain, unless removed, amounts of
homopolymers of repeating units of the first and/or second
polymer-forming materials. It is not always desirable or
necessary to remove such homopolymers from the resulting
25 block copolymer. Surprisingly, it has been found that the
block copolymers produced act as compatabilizers for the
homopolymers, such that the resultant mixture is
substantially uniform in appearance and properties.

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Suitable polymerization reactors include batch reactors such as continuously stirred tank reactors, continuous reactors such as single or twin-screw extruders, and combinations of batch and continuous reactors. Reactors

5   capable of high energy mixing, such as twin-screw extruders, are particularly useful as polymerization reactors in the present invention. Such extruders allow for continuous polymerization and more accurate temperature control over the polymerization than typical batch

10   polymerization reactors, particularly when the polymerization reaction is exothermic. Extruders are further preferred as polymerization reactors because they are capable of operation with very low to very high viscosity polymer melts.

15   Polymer-forming materials which are suitable for use in the present invention include those polymer-forming materials which form hard or soft polymer segments when polymerized. Preferred for use as a first polymer-forming material in the present invention are materials which form

20   soft or rubbery segments when polymerized, such as those materials having glass transition temperatures (T_g) less than about 10°C, and preferably less than about 0°C. Such first polymer-forming materials include, but are not limited to, alkylene oxides, trimethylene carbonates,

25   lactones, and mixtures thereof. More preferred first polymer-forming materials are trimethylene carbonate, ethylene glycol and lactones, including, but not limited to

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ε-caprolactone, δ-valerolactone, p-dioxanone and mixtures thereof.

Even more preferred as a first polymer-forming material are pre-copolymer materials, particularly when it

5   is desired to control the physical and chemical properties of the environmentally degradable block copolymers synthesized. For example, a pre-copolymer material can comprise a first polymer-forming material and an additional polymer-forming material such that when polymerized, the

10 first polymer is a copolymer having reduced crystallinity relative to a homopolymer of the first polymer-forming material. As a result, environmentally degradable block copolymers formed using the pre-copolymer as a first polymer forming material generally have different

15 properties than those environmentally degradable block copolymers having the same overall molar ratio of polymer-forming materials, but were not synthesized using the pre-copolymer. Further, in some instances the block copolymers synthesized using pre-copolymer materials have

20 characteristics which cannot be attained by synthesizing block copolymers from the same constituents without first forming the pre-copolymer material. Accordingly, the use of a pre-copolymer is very important in synthesizing block copolymers with desired characteristics.

25 The described ability to control the properties of the synthesized block copolymers using varying amounts of the constituent polymer-forming materials and pre-copolymer materials is illustrated in Figures 1-3. Figures 1-3 are

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graphical representations of the tensile strength, tensile modulus, and percent elongation, respectively, for various overall compositions of environmentally degradable block copolymer of ϵ-caprolactone and lactide synthesized using

5   a pre-copolymer of ϵ-caprolactone:lactide having a molar ratio of 80:20. Figures 4-6 are graphical representations of the tensile strength, tensile modulus, and percent elongation, respectively, for various overall compositions of environmentally degradable block copolymer of ϵ-

10   caprolactone and lactide synthesized without using a pre-copolymer as the first polymer-forming material. As can be seen from a comparison of Figures 1 and 4, for the same overall molar ratios of ϵ-caprolactone:lactide, the two environmentally degradable block copolymers have very

15   different tensile strengths. At about a 40 mole% ϵ-caprolactone content, the block copolymer in Figure 1 has a tensile strength of about 3,000 psi compared to a tensile strength of about 5,000 psi for the block copolymer in Figure 4. As can be seen from a comparison of Figures 2

20   and 5, for the same overall molar ratios of ϵ-caprolactone:lactide, the two environmentally degradable block copolymers have very different moduli. At about a 40 mole% ϵ-caprolactone content, the block copolymer in Figure 2 has a tensile modulus of about 46 kpsi compared to a

25   tensile modulus of about 180 kpsi for the block copolymer in Figure 5. Similarly, as can be seen from a comparison of Figures 3 and 6, for the same overall molar ratios of ϵ-caprolactone:lactide, the two environmentally degradable

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block copolymers have very different percent elongation. At about a 32 mole% ε-caprolactone content, the block copolymer in Figure 3 has a percent elongation of about 130% compared to a percent elongation of about 380% for the
5   block copolymer in Figure 6.

     Also illustrated by Figures 2 and 5, is that through the use of a pre-copolymer when synthesizing block copolymers, the constituent polymer materials can be used more efficiently to produce desired characteristics in the
10   resultant block copolymer. For example, at about 40 mole% ε-caprolactone content, the block copolymer synthesized using a pre-copolymer in Figure 2 has a tensile modulus within the range of from about 40 kpsi to about 50 kpsi. By comparison, the block copolymer in Figure 5, even at
15   about 50 mole% ε-caprolactone content, does not have a tensile modulus within the range of from about 40 kpsi to about 50 kpsi. Accordingly, when softness is a desired characteristic in the block copolymer, less ε-caprolactone needs to be used to achieve the desired characteristics
20   when a pre-copolymer is used to synthesize the block copolymer.

     Preferred for use as pre-copolymer materials include, but are not limited to, mixtures of cyclic esters of hydroxycarboxylic acids with alkylene oxides, trimethylene
25   carbonates and lactones. More preferred for use as pre-copolymer materials include, but are not limited to, mixtures of cyclic esters of hydroxycarboxylic acids with trimethylene carbonate, ethylene glycol and lactones,

including, but not limited to, ε-caprolactone, δ-valerolactone and p-dioxanone. Preferred cyclic esters of hydroxycarboxylic acids include, but are not limited to, lactide and glycolide. Examples of other suitable cyclic
5   esters include certain of the cyclic esters disclosed in copending U.S. Patent Application Serial No. 08/127,907, entitled "DEGRADABLE POLYDIOXANEONE-BASED MATERIALS". Even more preferred for use as pre-copolymer materials include, but are not limited to, mixtures of lactide with ε-
10   caprolactone.

When lactide and ε-caprolactone are used to form a random copolymer as the first polymer, it is desirable to combine lactide with the ε-caprolactone in amounts up to about 40 mole%, and preferably in amounts in the range of
15   from about 20 mole% to about 25 mole%. Concentrations above about 40 mole% lactide in the copolymer raises the glass transition temperature of the copolymer above about 0°C, making it less desirable as a first polymer when softness of the resultant block copolymer is desired.

20   To enhance the polymerization rate of the first polymer-forming material, a catalyst is added to the first polymer-forming material in the polymerization reactor. The term "catalyst," as used herein, refers to metal-containing compounds which are capable of increasing the
25   polymerization rate of a polymer-forming material. Although the term "catalyst" typically refers to materials which are not consumed in a chemical reaction, the term "catalyst" is used herein even though is not currently understood whether

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the described metal-containing compounds are consumed in the polymerization reaction.

Typically, the catalyst which is used depends upon the choice of the polymer-forming material with which it will

5   be combined.   For example, it is desirable to use a catalyst which is compatible with the polymer-forming material and does not substantially degrade the polymer-forming material or the polymers formed from such materials during processing.   Additionally, it is desirable to use a

10   catalyst which is non-toxic.   Suitable catalysts include, but are not limited to, tin, aluminum, yttrium and lanthanum based metal catalysts.   Preferred for use as catalysts are stannous octoate $(Sn(Oct)_2)$, yttrium or lanthanide series rare earth metal catalysts as are

15   described in U.S. Patent No. 5,028,667 by McLain et al., issued July 2, 1991, and mixtures thereof. More preferred for use as a catalyst is stannous octoate.

The amount of the catalyst to be combined with the first polymer-forming material can depend upon the amount

20   of the first polymer-forming material present, the toxicity of the catalyst in a finished product and in the environment after degradation of the product and to what extent, if any, the catalyst can degrade the polymers produced if too much catalyst is present during processing

25   of the polymers.   In most cases, the amount of catalyst added to the first polymer-forming material is less than about 1,000:1 moles first polymer-forming material:moles catalyst, preferably less than about 2,000:1 moles first

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polymer-forming material:moles catalyst, and more preferably less than about 2,500:1 moles first polymer-forming material:moles catalyst.

To further enhance the polymerization rate of the
5   first polymer-forming material and initiate the formation of the environmentally degradable block copolymers, a polymerization accelerant is also combined with the first polymer-forming material and catalyst in the polymerization reactor. The phrase "polymerization accelerant," as used
10   herein, refers to compounds which act as polymerization initiators (i.e., those compounds capable of providing chain propagating centers), thereby also accelerating the rate of polymerization, and are consumed in the polymerization reaction.

15   Typically, the polymerization accelerant which is used depends upon the choice of the polymer-forming material and catalyst with which it will be combined. For example, it is desirable to use a polymerization accelerant which is compatible with the polymer-forming material and catalyst
20   and does not substantially degrade or assist in the degradation of the polymer-forming material or the polymers formed from such materials, such as during processing. Additionally, it is desirable to use a polymerization accelerant which is non-toxic. Further, the type of block
25   copolymers produced, branched or star-shaped, is determined by the polymerization accelerant used. Accordingly, the choice of polymerization accelerant can also depend upon the type of block copolymer desired.

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Suitable polymerization accelerants include, but are not limited to, hydrogen-labile compounds such as alcohols, amino alcohols, diols, polyols, monoamino compounds, polyamino compounds and mixtures thereof. Preferred

5   polymerization accelerants are polyols, including, but not limited to, glycerol, poly(ϵ-caprolactone) triol and mixtures thereof. In general, star-shaped block copolymers are produced when polyols are used as the polymerization accelerant.

10   The type and amount of the polymerization accelerant to be combined with the first polymer-forming material can depend upon the desired final number average molecular weight (M_n) and weight average molecular weight (M_w) of the synthesized environmentally degradable block copolymers.

15   It has been found that the polymerization accelerant can affect the M_n and M_w of the resulting environmentally degradable block copolymers. While not fully understood, the effect of the polymerization accelerant on the M_n and M_w of the synthesized block copolymers appears to be dependent

20   upon the number of chain propagating centers on a single molecule of a polymerization accelerant. While not intending to be bound by theory, it is believed that the greater the number of chain propagating centers on a single molecule of a polymerization accelerant, the higher the

25   final M_n and M_w of the resulting environmentally degradable block copolymers. For example, when polyols are used as the polymerization accelerant and the propagating centers are the OH groups on the accelerant molecules, it is

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observed that for a given hydroxyl ([OH]) group concentration, the M_n and M_w of the resulting block copolymers are higher than for block copolymers synthesized using an alcohol as a polymerization accelerant.

5   In most cases, the amount of polymerization accelerant added to the first polymer-forming material is less than about 200:1 moles first polymer-forming material:moles polymerization accelerant, preferably less than about 300:1 moles first polymer-forming material:moles polymerization

10   accelerant, and more preferably less than about 500:1 moles first polymer-forming material:moles polymerization accelerant.

Polymerization of the first polymer-forming material can be carried out at a suitable temperature and pressure

15   to obtain a first polymer material. It is desirable, however, that the temperature of the polymerization reaction be maintained within a temperature range which minimizes degradation of and color formation in the polymer being produced. Typically, such polymerization temperatures

20   are within the range of about 150°C to about 210°C. Preferred temperature ranges can depend upon the polymer-forming material being polymerized and the polymerization accelerant being used. In most cases, however, it is preferred that the polymerization temperature be maintained

25   within the range of about 160°C to about 200°C, and more preferably at a temperature within the range of about 170°C to about 190°C. If desired, the polymerization reaction can be carried out under inert atmospheric conditions, such

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as under a blanketing gas, to prevent moisture contamination which degrades the polymers being produced and to prevent contact of the polymerization mass with oxygen which can oxidize the polymers being produced. Such
5 blanketing gases include, but are not limited to argon and nitrogen.

The time required for substantial completion of the first polymerization reaction depends upon the polymerization rate for the first polymer-forming material,
10 which in turn depends upon the polymerization reaction parameters, including, but not limited to the catalyst used, the polymerization accelerant used and the polymerization temperatures and pressures. A convenient method of determining the extent of completion of the
15 polymerization reaction is by measuring the melt viscosity of the polymerization mass in the polymerization reactor. When maximum melt viscosity is achieved, the polymerization reaction is typically complete. Typically, the time it takes for a first polymer-forming material to reach maximum
20 melt viscosity is within the range of about 10 minutes to about 65 minutes, preferably the time it takes for a first polymer-forming material to reach maximum melt viscosity is within the range of about 10 minutes to about 40 minutes, and more preferably the time it takes for a first polymer-
25 forming material to reach maximum melt viscosity is within the range of about 10 minutes to about 30 minutes.

An important feature of the first polymerization step is that the chains of the first polymer formed during

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polymerization are "living," i.e., they are reactive and able to continue to be polymerized. As a result, block copolymers can be formed by combining the first polymer with a second polymer-forming material. Accordingly, after

5 the first polymer material has been synthesized, a second polymer-forming material can be added to the first polymer in the same or an additional polymerization reactor. Though not necessary, it is desirable that the second polymer-forming material be capable of being polymerized at or near

10 about the same polymerization parameters (i.e., temperatures, pressures, etc.) as the first polymer-forming material. It is also desirable that the second polymer-forming material is not substantially degradable by the catalyst or polymerization accelerant utilized in

15 conjunction with the polymerization of the first polymer-forming material.

Polymer-forming materials which are suitable for use in the present invention as a second polymer-forming material include those polymer-forming materials which form

20 hard or soft polymer segments when polymerized. Preferred for use as second polymer-forming materials in the present invention are polymers which form hard segments when polymerized. Such second polymer-forming materials include, but are not limited to cyclic esters of hydroxycarboxylic

25 acids. More preferred materials for use in the present invention as second polymer-forming materials include lactide and glycolide. Even more preferred for use in the present invention as a second polymer-forming material is

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lactide. As used herein, the term "lactide" refers to the various isomeric forms of lactide, including, L-lactide, D-lactide, L,D-lactide and meso-lactide (M-lactide). When lactide is used as a second polymer-forming material, the

5   amounts of the various isomeric forms of lactide used can be varied to control the stereoregularity of the polylactide segments in the synthesized environmentally degradable block copolymers. Alternatively, the second polymer-forming material can also include up to about 5

10   mole% ϵ-caprolactone.

The amount of the second polymer-forming material added to the polymerization reactor depends upon the characteristics that are desired in the block copolymers to be produced. For example, to increase the elastomeric and

15   percent elongation qualities of the preferred environmentally degradable block copolymers of lactide and ϵ-caprolactone, it is desirable to increase the molar content of the ϵ-caprolactone to greater than about 5 mole% relative to lactide in the resulting block copolymer.

20   Preferably, however, the environmentally degradable block copolymers of lactide and ϵ-caprolactone contain in the range of from about 10 mole% to about 75 mole% ϵ-caprolactone. In general, to create a true block copolymer, enough of each polymer forming material must be added to

25   the polymerization reactor for the resulting block copolymers to contain greater than about 5 mole%, and preferably greater than about 10 mole%, of each polymer-forming material.

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Similar to the first polymerization reaction, a catalyst, as previously described is combined with the second polymer-forming material in order to enhance the rate of production of block copolymers. In a preferred

5 embodiment of the present invention, the catalyst combined with the second polymer-forming material is an additional amount of the same catalyst combined with the first polymer-forming material.

The amount of the catalyst to be combined with the

10 second polymer-forming material depends upon similar criteria used to determine the amount of catalyst combined with the first polymer-forming material, as previously described. In addition, consideration as to the type and concentration of catalyst already present in the first

15 polymer can effect the determination as to the amount of catalyst to be combined with the second polymer-forming material. In most cases, the amount of catalyst combined with the second polymer-forming material is less than about 1,000:1 moles second polymer-forming material:moles

20 catalyst, preferably less than about 2,000:1 moles second polymer-forming material:moles catalyst, and more preferably less than about 4,000:1 moles second polymer-forming material:moles catalyst.

A polymerization accelerant, as described previously,

25 is also combined with the second polymer-forming material in the polymerization reactor. In a preferred embodiment of the present invention, the polymerization accelerant combined with the second polymer-forming material and

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catalyst is an additional amount of the same polymerization accelerant combined with the first polymer-forming material.

The amount of the polymerization accelerant to be combined with the second polymer-forming material depends upon similar criteria used to determine the amount of polymerization accelerant combined with the first polymer-forming material, as previously described. However, additional consideration must be given as to the type and concentration of polymerization accelerant and catalyst already present in the first polymer, because these factors can effect the determination as to the amount of polymerization accelerant to be combined with the second polymer-forming material. In most cases, the amount of polymerization accelerant added to the polymerization reactor and combined with the second polymer-forming material is less than about 200:1 moles second polymer-forming material:moles polymerization accelerant, preferably less than about 300:1 moles second polymer-forming material:moles polymerization accelerant, and more preferably less than about 500:1 moles second polymer-forming material:moles polymerization accelerant.

After combining the second polymer-forming material and a polymerization accelerant in the polymerization reactor with the first polymer, polymerization can be carried out at a suitable temperature and pressure to obtain a block copolymer material. It is desirable, however, that the temperature and pressure of the

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polymerization reaction be maintained within temperature and pressure ranges which minimize degradation of and color formation in the block copolymer being produced. Typically, such polymerization temperatures are within the range of

5   about 150°C to about 210°C. Preferred temperature ranges can depend upon the polymer-forming material being polymerized and the polymerization accelerant being used. In most cases, however, it is preferred that the polymerization temperature be maintained within the range

10   of about 160°C to about 200°C, and more preferably at a temperature within the range of about 170°C to about 190°C. If desired, the polymerization reaction can be carried out under inert atmospheric conditions, such as under a blanketing gas, to prevent moisture contamination which

15   degrades the polymers being produced and to prevent contact of the polymerization mass with oxygen which can oxidize the polymers being produced. Such blanketing gases include, but are not limited to argon and nitrogen.

The time required for the block copolymerization

20   reaction to go to substantial completion depends upon the polymerization rate for the second polymer-forming material, which in turn depends upon the polymerization reaction parameters, including, but not limited to the polymerization accelerants and catalysts used and the

25   polymerization temperatures.   As stated previously, a convenient method of determining the extent of completion of the polymerization reaction is by measuring the melt viscosity of the polymerization mass in the polymerization

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reactor, and when maximum melt viscosity is achieved, the polymerization reaction is typically complete. Typically, the time it takes for the block copolymer mass to reach maximum melt viscosity is within the range of about 30

5   minutes to about 120 minutes, preferably is within the range of about 30 minutes to about 100 minutes, and more preferably is within the range of about 30 minutes to about 90 minutes. Accordingly, the total amount of time it takes to produce the environmentally degradable block copolymers

10   is typically within the range of from about 40 minutes to about 170 minutes, preferably within the range of from about 40 minutes to about 130 minutes, and more preferably within the range of about 40 minutes to about 120 minutes.

The time with which it takes in order to produce block

15   copolymers according to the present invention is an important aspect of the present invention. In contrast to known processes for producing block copolymers, the method described herein allows for the economical production of block copolymers due to the increased reaction rates, and

20   without significant loss in weight average or number average molecular weight of the resulting block copolymer. The resulting reduced reaction times allow for the production of a final block copolymer that has substantially no color formation.

25   Typically, the conversion of the polymer-forming materials during polymerization of the block copolymers is in the range of from about 90% to about 98%, and preferably in the range of from about 92% to about 98%. As a result

of the high conversion of the polymer-forming materials, little of the polymer-forming materials are wasted. Further, less of the polymer-forming materials remain in the synthesized block copolymer which may need to be
5   removed.

In general, the environmentally degradable block copolymers synthesized have number average molecular weights (M_n) in the range of from about 60,000 to about 150,000 and weight average molecular weights (M_w) in the
10   range of from about 120,000 to about 300,000. In addition, such block copolymers typically exhibit at least two glass transition temperatures (T_g) which are representative of each of the polymers which comprise the block copolymer.

Following synthesis according to the methods of the
15   present invention, the environmentally degradable block copolymers can be treated in order to remove residual monomers and other impurities in the environmentally degradable block copolymers in order to render them suitable for their intended use. Such treatments include,
20   but are not limited to grinding of the block copolymer mass and subsequently drying the ground block copolymer mass to evolve undesired contaminants. In one embodiment of the present invention, the block copolymers synthesized can be dried for a time period within the range of from about 0.5
25   hours to about 20 hours at a temperature within the range of from about 100°C to about 180°C and a pressure within the range of from about 0.1 torr to about 5 torrs to remove residual monomers from the block copolymer mass. In another

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embodiment of the present invention, an extruder is used to continuously produce the environmentally degradable block copolymers and devolatilization of the monomers from the polymerization mass is accomplished using a

5   devolatilization zone in the reactor itself as is taught in the art, i.e., through the use of vents and reduced pressures in the extruder.

Importantly, the physical properties of the environmentally degradable block copolymers produced varies

10   widely and can be selectively controlled, as previously described. As a result, the environmentally degradable block copolymers synthesized according to the method of the present invention are suitable for use as a substitute for other, environmentally non-degradable polymers, including,

15   but not limited to, high density polyethylene, low density polyethylene, and polyvinyl chloride. For example, as shown in Figure 2, a degradable block copolymer of about 60 mole% lactide and about 40 mole% ϵ-caprolactone, synthesized using a pre-copolymer of lactide and ϵ-caprolactone has a

20   tensile modulus of about 40 kpsi to about 50 kpsi, which is within the range of the tensile moduli for high density polyethylene (about 60 kpsi) and low density polyethylene (about 30 kpsi).

In addition to the synthesis and purification of the

25   environmentally degradable block copolymers, the synthesized block copolymers can be further processed using conventional polymer processing techniques to obtain a product, such as, plastic bags, packaging films and solid

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cast, molded or extruded articles. It is preferred, however, that the environmentally degradable block copolymers synthesized according to the methods of the present invention can be injected, rolled, blown, cast or
5   pressed into films for use as plastic bags and packaging materials. As a result of the high melt strength which can be obtained with star-shaped environmentally degradable polymers synthesized according to the present invention, the block copolymers of the present invention are
10 particularly well-suited for use in blow molding applications.

    Reference is now made to the following examples, which are intended to illustrate, and not to limit the present invention. Unless otherwise noted, all reaction times
15 given are for the polymerization to go to completion, which was estimated to be when the polymerization mass reached maximum melt viscosity. In addition, the residual monomer contents of the polymerization masses were determined by gas chromatography, and the M_n and M_w of the environmentally
20 degradable block copolymers were obtained by gel permeation chromatography.

                            EXAMPLES

COMPARATIVE EXAMPLE 1:

25   The following comparative example illustrates the production of an environmentally degradable block copolymer of ϵ-caprolactone and a lactide without use of a polymerization accelerant in the second polymerization step.

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ε-caprolactone, purchased from Aldrich Chemical Company was distilled in a vacuum over CaH$_2$ and stored in an argon gas environment. A 140 g sample of the ε-caprolactone thus prepared was charged to a Haake Rheomix 3000

5   polymerization reactor along with 0.275 g of stannous octoate, Sn(Oct$_2$) obtained from Sigma Chemical Company, to give a molar ratio of ε-caprolactone:stannous octoate of about 1,472:1, and was reacted at 180°C and atmospheric pressure using a mixing rate of 36 rpm.   During the

10   polymerization reaction, 9 g of polymer samples were taken from the reactor for analysis.

After 25 minutes, when the melt viscosity reached its maximum, L-lactide purchased from Purac Biochem, Gorinchem (Holland), which had been stored in an argon gas

15   environment after purchase, was added to the polymerization reactor in order to give a polymerization mass concentration of ε-caprolactone of about 35.7 mole% and a total polymer:catalyst molar ratio of 4,280:1, based on total ε-caprolactone and lactide.   The reaction was

20   continued at the same temperature, pressure and mixing rate for an additional 110 minutes, until the melt viscosity reached its maximum.   The resulting block copolymer had an ε-caprolactone concentration of 36.7 mole% (obtained through NMR analysis).   The block copolymer produced was

25   pale yellow in color.

Table 1 below lists the results of the block copolymerization. The block copolymerization took a total of 135 minutes. The rate of lactide polymerization is shown graphically in Figure 7.

TABLE 1

| Reactor Feed | Time (Minutes) | Residual Monomer (wt%) | | M_n | M_w |
		ε-caprolactone	Lactide		
ε-Caprolactone & Sn(Oct)₂	10	23.37	-	86,065	151,925
	15	7.71	-	86,956	171,826
	20	4.64	-	78,641	166,939
	25	3.14	-	89,726	164,363
L-Lactide Added	55	0.90	40.44	111,959	174,944
	70	0.87	29.31	109,234	184,038
	95	0.67	13.71	122,390	201,975
	110	0.56	5.19	109,190	197,654

EXAMPLE 2:

The following example illustrates the increased polymerization rate of the second polymer-forming material obtainable by the addition of catalyst and polymerization accelerant in the second polymerization step according to the present invention.

A 124.2 g sample of ε-caprolactone prepared as described in the Example 1 was charged to a Haake Rheomix 3000 polymerization reactor along with stannous octoate to give a molar ratio of ε-caprolactone:stannous octoate of about 3000:1. The ε-caprolactone was polymerized in the polymerization reactor at a temperature of 180°C and atmospheric pressure using a mixing rate of 36 rpm. During the polymerization, 14 g of polymer samples were taken from the reactor for analysis.

After 32 minutes, L-lactide, was added to the polymerization reactor to give total concentration of ε-caprolactone in the polymerization mass of about 35.7 mole%. At the same time, stannous octoate and poly(ε-caprolactone) triol were added to the polymerization reactor in a molar ratio of monomer:stannous octoate:[OH] concentration (based onpoly(ε-caprolactone) triol) of about 5,000:1:6. Polymerization was continued at the same temperature, pressure and mixing rate for an additional 53 minutes. The ε-caprolactone concentration in the resulting block copolymer was measured to be 36.5 mole% (by NMR analysis) and the total molar ratio of monomer:stannous octoate:[OH] concentration was 4,038/1/2.2, based on total

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ε-caprolactone and lactide.   The block copolymer produced
was colorless.

        The results of the polymerization are shown below in
Table 2.   The overall block copolymerization took about 83
5   minutes.   The   rate   of   lactide   polymerization   is   shown
graphically in Figure 7. The rate of lactide polymerization
in this Example 2 is greatly enhanced relative to the rate
of lactide polymerization for Comparative Example 1 due to
the addition of polymerization accelerant in the second
10   polymerization in Example 2.

TABLE 2

Reactor Feed	Time (Minutes)	Residual Monomer (wt%)		M_n	M_w
		ε-caprolactone	Lactide		
ε-Caprolactone & Sn(Oct)₂	30	13.97	-	61,945	126,074
L-Lactide & Sn(Oct)₂ & Poly(ε-caprolactone) triol Added	18	3.15	24.89	101,929	152,727
	28	2.91	13.92	90,143	158,325
	43	2.62	7.48	106,944	171,975
	53	2.27	5.01	89,289	162,821

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EXAMPLE 3:

The following example illustrates the increased polymerization rate of the second polymer-forming material obtainable by the addition of catalyst and polymerization
5   accelerant in the second polymerization step according to the present invention.

A 110 g sample of ϵ-caprolactone prepared as described in Example 1 was charged to a Haake Rheomix 3000 polymerization reactor along with stannous octoate to give
10   a molar ratio of ϵ-caprolactone:stannous octoate of about 3,000:1. The ϵ-caprolactone was polymerized in the polymerization reactor at a temperature of 180°C and atmospheric pressure using a mixing rate of 36 rpm. During the polymerization, 5 g of polymer samples were taken from
15   the reactor for analysis.

After 36 minutes, L-lactide, was added to the polymerization reactor to give total concentration of ϵ-caprolactone in the polymerization mass of about 35.7 mole%. At the same time, stannous octoate and glycerol
20   were added to the polymerization reactor in a molar ratio of monomer:stannous octoate:[OH] concentration (based on glycerol) of about 5,000/1/9. Polymerization was continued at the same temperature, pressure and mixing rate for an additional 54 minutes. The ϵ-caprolactone concentration in
25   the resulting block copolymer was measured to be 37.8 mole% (by NMR analysis) and the total molar ratio of monomer: stannous octoate:[OH] concentration was 4,032/1/3.2, based

on total ε-caprolactone and lactide.   The block copolymer
produced was colorless.

The results of the polymerization are shown below in
Table 3.   The total block copolymerization took about 89
5   minutes.   The rate of lactide polymerization is shown
graphically in Figure 7. The rate of lactide polymerization
in this Example 3 is greatly enhanced relative to the rate
of lactide polymerization for Comparative Example 1 due to
the addition of polymerization accelerant in the second
10 polymerization in Example 3.

TABLE 3

Reactor Feed	Time (Minutes)	Residual Monomer (wt%)		M_n	M_w
		ε-caprolactone	Lactide		
ε-Caprolactone & Sn(Oct)$_2$	35	13.69	-	74,038	131,473
L-Lactide & Sn(Oct)$_2$ & Glycerol Added	24	3.26	15.12	81,278	138,158
	49	3.12	3.12	99,654	154,905
	54	1.86	2.60	77,927	143,915

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COMPARATIVE EXAMPLE 4:

The following comparative example illustrates the properties of an environmentally degradable block copolymer having an ϵ-caprolactone concentration of about 50 mole%.

5   A 150.4 g of ϵ-caprolactone prepared as described in Example 1 was charged to a Haake Rheomix 3000 polymerization reactor along with stannous octoate and glycerol to give a molar ratio of monomers:stannous octoate:[OH] concentration (based on glycerol) of about

10   3,000/1/7.5. The ϵ-caprolactone monomer was polymerized at 180°C and at atmospheric pressure using a mixing rate of 35 rpm. During this period of polymerization, about 6 g of samples were taken for analysis.

After 22 minutes, 179.5 g of L-lactide was added to

15   the polymerization reactor to give a total concentration of ϵ-caprolactone in the polymerization mass of about 50 mole%. Polymerization was continued at the same temperature, pressure and mixing rate for an additional 115 minutes. The ϵ-caprolactone concentration in the resulting

20   block copolymer was measured to be 51.1 mole% (by NMR analysis) and the total molar ratio of monomers:stannous octoate:[OH] concentration was 6,000/1/3.8. The results of polymerization are shown below in Table 4. The block copolymer produced was pale yellow in color.

25   The entire block copolymerization took about 180 minutes. The block copolymer exhibited a T_g at -52.4°C, corresponding to the glass transition of the poly(ϵ-caprolactone) soft phase. The polylactide hard phase of

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the block copolymer exhibited a melting temperature of
140.1°C with ΔH of 22.74 J/g, measured by differential
scanning calorimeter.   The melting peak of soft phase
overlapped the T_g of the hard phase; both were at about
5   50°C.   Tensile testing of the block copolymer yielded the
following: tensile modulus, 161 kpsi; stress at break,
5536 psi; elongation at break, 624%.

TABLE 4

Reactor Feed	Time (Minutes)	Residual Monomer (wt%)		M_n	M_w
		ε-caprolactone	Lactide		
ε-caprolactone, Sn(Oct)$_2$, glycerol	10	14.16		59,429	103,077
	16	2.54		57,962	118,270
	22	1.34		64,961	118,353
L-Lactide added	43	0.46	48.05	60,501	122,900
	68	0.45	33.36	73,253	132,430
	98	0.45	15.9	83,654	144,448
	138	0.45	11.33	90,151	167,125
	158	0.48	5.28	90,145	163,974

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EXAMPLE 5:

The following example illustrates the synthesis of an environmentally degradable block copolymer with an overall feed ε-caprolactone concentration of about 50 mole%, and
5 synthesized using an 80:20 molar ratio mixture of ε-caprolactone:L-lactide as the first polymer-forming material.

A mixture of 152.68 g of ε-caprolactone prepared as described in Example 1 and 48 g of L-lactide, resulting in
10 a mixture of ε-caprolactone:L-lactide having the molar ratio 80:20, was charged to a Haake Rheomix 3000 polymerization reactor along with stannous octoate and glycerol to give a molar ratio of monomers:stannous octoate:[OH] concentration (based on glycerol) of about
15 4,240/1/6.6.   The monomers were polymerized at 180°C and atmospheric pressure using a mixing rate of 36 rpm to form a random copolymer of ε-caprolactone and L-lactide. During this period of polymerization, about 10 g of sample was taken for analysis.

20   After 65 minutes, 136 g of L-lactide was added to the polymerization reactor to give a total concentration of ε-caprolactone in the polymerization mass of about 50 mole%. At the same time, stannous octoate and glycerol were added to the reactor in a molar ratio of monomers:stannous
25 octoate:[OH] concentration of about 4,250/1/8.8. Polymerization was continued at the same temperature, pressure and mixing rate for an additional 35 minutes. The ε-caprolactone concentration in the resulting block

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copolymer was measured to be 49.4 mole% (by NMR analysis) and the total molar ratio of monomers:stannous octoate:[OH] concentration was 4,245/1/7.5.   The results of polymerization are shown below in Table 5.   The block copolymer
5   produced was colorless and nearly transparent, probably as a result of the reduced crystallinity of the soft phase.

The block copolymerization took about 100 minutes. The block copolymer showed two T_g's at -36.3 and 52.1°C, corresponding   to   the   glass   transitions   of   the ϵ-
10   caprolactone-rich soft phase and the L-lactide-rich hard phase, respectively. A melting temperature of 159.6°C with ΔH of   6.49   J/g,   measured   by   differential   scanning calorimeter corresponds to the melting point of the hard phase. The melting peak of the soft phase was not observed
15   because the crystallinity of the poly(ϵ-caprolactone) in the   soft   phase   was   substantially   reduced   by copolymerization with 20 mole% L-lactide.   Tensile testing was conducted with the following results: Young's tensile modulus, 11.3 kpsi; stress at break, 1712 psi; elongation
20   at break, 620%.

Notably, the overall ϵ-caprolactone concentrations are nearly the same for the block copolymers synthesized in Examples 4 and 5.   However, the block copolymer formed in Example 5 was much softer than that formed in Example 4,
25   with Young's tensile modulus of 11.3 kpsi and 161 kpsi, respectively.   The differences in the moduli are probably also due to the elimination of crystallinity of the soft phase in Example 5.

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TABLE 5

Reactor Feed	Time (Minutes)	Residual Monomer (wt%)		M_n	M_w
		ε-caprolactone	Lactide		
ε-caprolactone, L-lactide, Sn(Oct)$_2$, glycerol	35	40.8	3.21	42,491	76,976
	45	23.49	1.80	54,688	110,735
	55	8.75	0.69	71,331	137,217
	65	3.84	0.62	70,775	140,546
L-lactide, Sn(Oct)$_2$, glycerol	10	1.81	12.93	81,021	139,928
	25	1.87	5.72	85,763	151,564
	35	1.67	5.20	81,282	147,171

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The foregoing disclosure of the present invention has been presented for purposes of illustration and description. The description is not intended to limit the invention to the form disclosed herein. Consequently, the
5   invention and modifications commensurate with the above teachings and skill and knowledge of the relevant art are within the scope of the present invention. The preferred embodiment described above is also intended to explain the best mode known of practicing the invention and to enable
10 others skilled in the art to utilize the invention in various embodiments and with the various modifications required by their particular applications for use of the invention. It is intended that the appended claims be construed to include all alternative embodiments as
15 permitted by the prior art.

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<u>What is claimed is</u>:

1.   A   method   for   synthesizing   environmentally degradable block copolymers, the method comprising the steps of:

5   (a) polymerizing a first polymer-forming material selected from the group consisting of lactones, cyclic esters of hydroxycarboxylic acids, trimethylene carbonates, alkylene oxides and mixtures thereof, in the presence of a first polymerization accelerant and a first catalyst to

10   form a first polymer;

(b) combining said first polymer with a second polymer-forming material selected from the group consisting of cyclic esters of hydroxycarboxylic acids and mixtures thereof and a second polymerization accelerant and a second

15   catalyst; and

(c) polymerizing said second polymer-forming material to form said environmentally degradable block copolymer.

2.   The method as claimed in Claim 1, wherein said environmentally degradable block copolymer has soft

20   segments of said first polymer and hard segments of a polymer comprising repeating units of said second polymer-forming material.

3.   The method as claimed in Claim 1, wherein said steps of polymerizing comprise melt polymerization.

25   4.   The method as claimed in Claim 3, wherein said step of melt polymerizing is accomplished using an extruder.

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5.   The method as claimed in Claim 4, wherein said extruder comprises a twin screw extruder.

6.   The method as claimed in Claim 1, wherein said second polymerization accelerant and said second catalyst comprise an additional amount of said first polymerization accelerant and said first catalyst.

7.   The method as claimed in Claim 1, wherein said first and second polymerization accelerants are selected from the group consisting of alcohols, amino alcohols, diols, polyols, monoamino compounds, polyamino compounds and mixtures thereof.

8.   The method as claimed in Claim 1, wherein said first and said second catalysts comprise a metal catalyst selected from the group consisting of tin, aluminum, yttrium and lanthanum based metal catalysts.

9.   The method as claimed in Claim 1, wherein said first   polymerization   accelerant   and   said   second polymerization accelerant are selected from the group consisting of glycerol and poly(ϵ-caprolactone) triol.

10.   The method as claimed in Claim 9, wherein said first catalyst and said second catalyst comprise stannous octoate.

11.   The method as claimed in Claim 1, wherein said first polymer-forming material comprises ϵ-caprolactone and said second polymer-forming material comprises lactide.

12.   The method as claimed in Claim 1, wherein said first polymer comprises a copolymer of a lactone and a cyclic ester of a hydroxycarboxylic acid.

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13. The method as claimed in Claim 1, wherein said first polymer-forming material comprises a copolymer of ϵ-caprolactone and lactide.

14. The method as claimed in Claim 13, wherein said second polymer-forming material comprises lactide.

15. The method as claimed in Claim 14, wherein said second polymer-forming material comprises L-lactide and D-lactide.

16. The method as claimed in Claim 1, wherein said second polymer-forming material comprises L-lactide and ϵ-caprolactone.

17. The method as claimed in Claim 1, wherein said first polymer-forming material comprises ϵ-caprolactone and said second polymer-forming material comprises glycolide.

18. The method as claimed in Claim 1, wherein said steps of polymerizing said first polymer-forming material and polymerizing said second polymer-forming material are carried out for a combined time of less than about 3 hours.

19. The method as claimed in Claim 1, wherein said steps of polymerizing said first polymer-forming material and polymerizing said second polymer-forming material are carried out at temperatures within the range of from about 150°C to about 210°C.

20. The method as claimed in Claim 1, wherein said environmentally degradable block copolymer comprises ϵ-caprolactone in the range of from about 5 mole% to about 50 mole%.

21.   The method as claimed in Claim 1, wherein said environmentally degradable block copolymer is selected from the group consisting of star-shaped and branched environmentally degradable block copolymers.

5   22.   The method as claimed in Claim 1, wherein said environmentally degradable block copolymer has a weight average molecular weight (M_w) in the range of from about 120,000 to about 300,000.

23.   The method as claimed in Claim 1, wherein said 10 environmentally degradable block copolymer has a number average molecular weight (M_n) in the range of from about 60,000 to about 150,000.

24.   The method as claimed in Claim 1, comprising the further step of manufacturing a blown film from said 15 environmentally degradable block copolymer.

25.   The method as claimed in Claim 1, wherein said environmentally degradable block copolymer is suitable for use as a substitute for other, non-degradable polymers selected from the group consisting of high density 20 polyethylene, low density polyethylene and polyvinyl chloride.

26.   A method for synthesizing environmentally degradable block copolymers, the method comprising the steps of:

25   (a)   melt polymerizing ϵ-caprolactone in the presence of a polymerization accelerant and a catalyst at a temperature within the range of from about 150°C to about

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210°C for a time period of less than about 65 minutes to form a poly(ε-caprolactone) polymer;

(b) mixing said poly(ε-caprolactone) polymer with an amount of a polymer-forming material selected from the
5   group consisting of lactide, glycolide and mixtures thereof and an additional amount of said polymerization accelerant and an additional amount of said catalyst, such that the resulting mixture comprises from about 50 mole% to about 95 mole% said polymer-forming material; and

10   (c) melt polymerizing said polymer-forming material at a temperature within the range of from about 150°C to about 210°C for a time period of less than about two hours to form an environmentally degradable block copolymer.

27. The method as claimed in Claim 26, wherein said
15   step of melt polymerizing is accomplished using a twin screw extruder.

28. The method as claimed in Claim 26, wherein said polymerization accelerant is selected from the group consisting of alcohols, amino alcohols, diols, polyols,
20   monoamino compounds, polyamino compounds and mixtures thereof.

29. The method as claimed in Claim 26, wherein said catalyst comprises a metal catalyst selected from the group consisting of tin, aluminum, yttrium and lanthanum based
25   metal catalysts.

30. The method as claimed in Claim 26, wherein said environmentally degradable block copolymer has a weight

average molecular weight (M_w) in the range of from about 120,000 to about 300,000.

31.   The method as claimed in Claim 26, wherein said environmentally degradable block copolymer has a number average molecular weight (M_n) in the range of from about 60,000 to about 150,000.

32.   The method as claimed in Claim 26, comprising the further step of manufacturing a blown film from said environmentally degradable block copolymer.

33.   The method as claimed in Claim 26, wherein said environmentally degradable block copolymer is suitable for use as a substitute for other, non-degradable polymers selected from the group consisting of high density polyethylene, low density polyethylene and polyvinyl chloride.

34.   The method as claimed in Claim 26, wherein said steps of melt polymerizing are carried out for a combined time of less than about 3 hours.

35.   A method for synthesizing environmentally degradable block copolymers, the method comprising the steps of:

(a) providing a first environmentally degradable polymer-forming material having a glass transition temperature of less than about 10°C to a polymerization reactor;

(b) polymerizing said environmentally degradable first polymer-forming material in the presence of a first

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catalyst and a first polymerization accelerant comprising a hydrogen-labile compound to form a first polymer;

(c) combining a second polymer-forming material comprising a cyclic ester of a hydroxycarboxylic acid with
5   said first polymer; and

(d) polymerizing said second polymer-forming material in the presence of a second polymerization catalyst and a second polymerization accelerant comprising a hydrogen-labile compound to form said environmentally degradable
10   block copolymer.

36. The method as claimed in Claim 35, wherein said first polymer-forming material comprises ε-caprolactone.

37. The method as claimed in Claim 35, wherein said cyclic ester of a hydroxycarboxylic acid comprises lactide.

15   38. The method as claimed in Claim 37, wherein said lactide comprises L-lactide and D-lactide.

39. The method as claimed in Claim 35, wherein said steps of polymerizing comprise melt polymerization.

40. The method as claimed in Claim 39, wherein said
20   step of melt polymerizing is accomplished using an extruder.

41. The method as claimed in Claim 35, wherein said second polymerization accelerant and said second catalyst comprise an additional amount of said first polymerization
25   accelerant and said first catalyst.

42. The method as claimed in Claim 35, wherein said first and second polymerization accelerants are selected from the group consisting of alcohols, amino alcohols,

diols, polyols, monoamino compounds, polyamino compounds, and mixtures thereof.

43.   The method as claimed in Claim 35, wherein said first and second polymerization accelerants comprise
5   polyols.

44.   The method as claimed in Claim 35, wherein said first and second catalysts comprise a metal catalyst selected from the group consisting of tin, aluminum, yttrium and lanthanum based metal catalysts.

10   45.   The method as claimed in Claim 35, wherein said environmentally degradable block copolymer comprises a block copolymer of ε-caprolactone and lactide.

46.   The method as claimed in Claim 35, wherein said environmentally degradable block copolymer comprises a
15   star-shaped environmentally degradable block copolymer.

47.   The method as claimed in Claim 35, comprising the further step of manufacturing a blown film from said environmentally degradable block copolymer.

48.   The method as claimed in Claim 35, wherein said
20   environmentally degradable block copolymer is suitable for use as a substitute for other, non-degradable polymers selected from the group consisting of high density polyethylene, low density polyethylene and polyvinyl chloride.
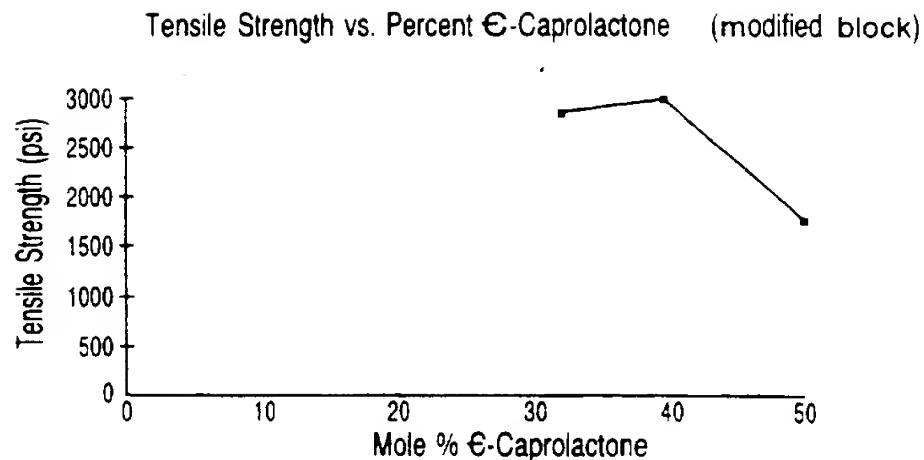
25   49.   An environmentally degradable block copolymer comprising from about 5 mole% to about 50 mole% hard segments of a polymer of ε-caprolactone and from about 50 mole% to about 95 mole% soft segments of a polymer having

repeating units of a material selected from the group consisting of lactide and glycolide, wherein said block copolymer is substantially colorless.

50. A plastic bag comprising the environmentally degradable block copolymer claimed in Claim 49.

51. The environmentally degradable block copolymer claimed in Claim 49, wherein said block copolymer is suitable for use as a substitute for other, non-degradable polymers selected from the group consisting of high density polyethylene, low density polyethylene and polyvinyl chloride.
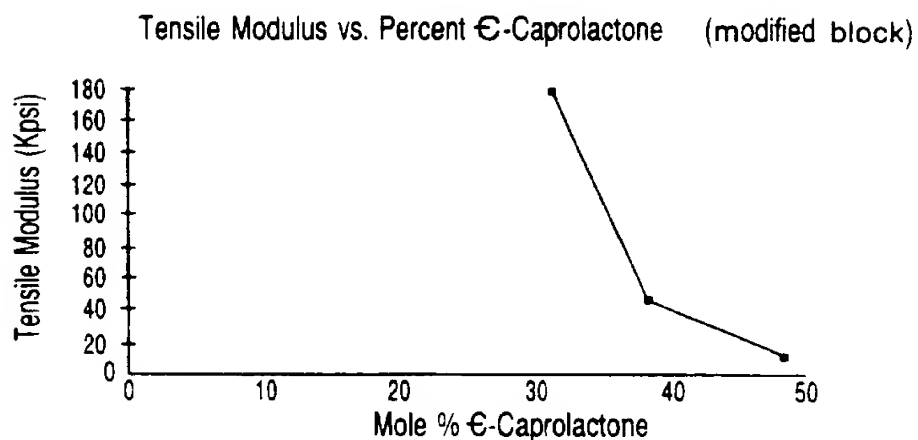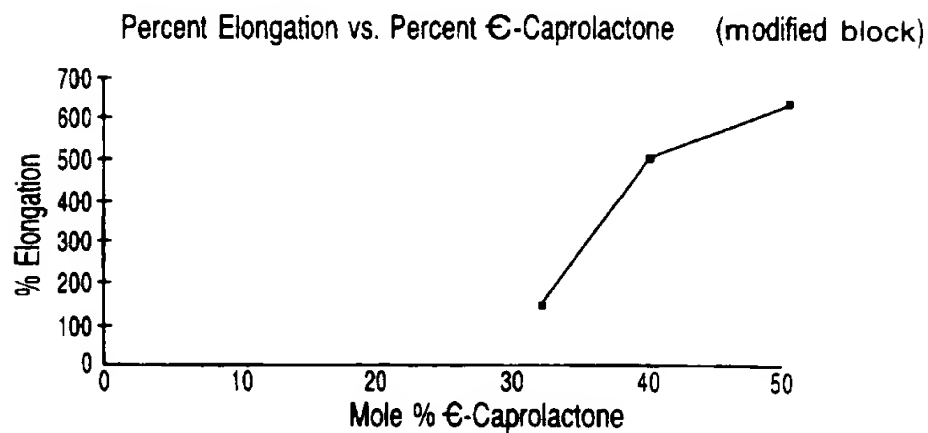
Tensile Strength vs. Percent Є-Caprolactone   (modified block)

Fig. 1

Tensile Modulus vs. Percent Є-Caprolactone   (modified block)

Fig. 2

Percent Elongation vs. Percent Є-Caprolactone   (modified block)

Fig. 3

SUBSTITUTE SHEET (RULE 26)

Tensile Strength vs. Percent Є-Caprolactone

Fig. 4

Tensile Modulus vs. Percent Є-Caprolactone

Fig. 5

Fig. 6

EFFECT OF CATALYST AND ACCELERANT ON LACTIDE POLYMERIZATION

Fig. 7

INTERNATIONAL SEARCH REPORT

	Intel. ional application No
	PCT/US96/16683

A.   CLASSIFICATION OF SUBJECT MATTER

IPC(6)   C08G 63/08, 63/02
US CL   :528/354, 355, 359, 361, 365, 370, 371
According to International Patent Classification (IPC) or to both national classification and IPC

B.   FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S   528/354, 355, 359, 361, 365, 370, 371

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C.   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, 5,080,665 A (JARRETT et al.) 14 January 1992, see column 6, line 14 through column 7, line 22 and Examples 1-9.	1-51

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

* Special categories of cited documents	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 NOVEMBER 1996	2 6 DEC 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer MELVYN I. MARQUIS
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2351

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